PYRROLE-DERIVED OLIGO- AND POLYSQUARAINES: SYNTHESIS, OPTICAL PROPERTIES AND CONDUCTIVITY STUDIES

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BY

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Dedicated To My Father

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CERTIFICATE

Certified that the work embodied in this thesis entitled: **"Pyrrole-Derived Oligo- and Polysquaraines: Synthesis, Optical Properties and Conductivity Studies"** has been carried out by Mr. C. R. Chenthamarakshan under my supervision and the same has not been submitted elsewhere for a degree.

A. Ajayaghosh
(Thesis Supervisor)

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of the investigations carried out by me at the Photochemistry Research Unit of the Regional Research Laboratory, Thiruvananthapuram under the guidance of Dr. A. Ajayaghosh and the same has not been submitted elsewhere for a degree.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

C. R. Chenthamarakshan

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May, 1997 C. R. Chenthamarakshan

PREFACE

Synthesis of π-conjugated oligomers and polymers and investigation of their optical, electronic and related properties constitute an important interdisciplinary area of organic-polymeric-material related research. Recently, several advances have been made in this area, some of which include the synthesis of soluble low bandgap polymers, self-acid-doped polymers and polymer-based sensors for metal ions. One of the central goals of these studies is the fundamental understanding of the structure-porperty relationships that might form the basis for the designing of novel materials with tailored properties. The present investigation is an attempt towards the designing of a new class of conjugated macromolecular materials based on an important class of organic dyes namely squaraine dyes. Squaraine dyes possess sharp and intense absorption in the visible and near infra red region. Due to the peculiar structural characteristics and charge-transfer interactions, these dyes show interesting optical and electronic properties which make them suitable for several technological applications. To fully harvest these properties, it would be appropriate to synthesize macromolecular analogues of squaraine dyes which allow the designing of novel materials for specific applications.

The main objectives of the present investigation were the synthesis and studies of squaraine dye based low bandgap polymers, self-doped conducting materials and metal ion sensors. Pyrrole-derived squaraine dyes have been chosen as the key materials for the present study due to the possibility of the extension of their structures to macromolecular level and their accessibility for structural modification with appropriate functional groups.

The first Chapter of the thesis consists of a brief review on the recent developments in the area of π-conjugated conducting polymer research. After giving a brief introduction to the theoretical aspects of conductivity, various routes for the synthesis of conducting polymers are briefly reviewed. Emphasis has been given to the recent developments in the field of low bandgap polymers, self-acid-doped conducting polymers and conjugated polymer based sensors. In addition, a brief introduction to squaraine dyes and the recent attempts toward the synthesis of their polymer analogues are presented.

Chapter 2 of the thesis describes the synthesis and studies of some soluble copolymers of alkyl substituted pyrroles and squaric acid. It has been observed that polycondensation of pyrrole derivatives with squaric acid under azeotropic reflux conditions in *n*-butanol-benzene mixture resulted in low molecular weight polysquaraines consisting mainly of 1,3-oriented zwitterionic repeat units whereas polycondensation in DMSO-acetic acid medium under room temperature gave copolymers comprising of both 1,3-oriented zwitterionic and 1,2-oriented diketonic repeat units. The latter polymers showed improved solubility, molecular weights and conductivity compared to those of the former polymers. Detailed analysis of their structures and evaluation of their properties such as solvatochromism, pH-dependent optical absorption changes and conductivity are presented.

The third Chapter of the thesis deals with the synthesis and properties of a new class of water soluble conducting materials based on pyrrole-derived squaraine dyes. The presence of covalently attached propane sulfonate groups in these materials enhanced their electrical conductivity without further doping. This is attributed to the intramolecular doping of the polymer by the pendent propane sulfonate groups. Several self-doped random co-oligomers were prepared and their optical and conducting properties were evaluated. In addition, effects of polymeric additives such as poly(vinylalcohol) and ploy(vinylpyrrolidone), on the conducting properties of the self-acid-doped squaraine oligomers are presented.

The last chapter of the thesis describes the synthesis, photophysical and metal ion binding properties of squaraine based molecular wires (oligomers) **14a** and **14b**. The photophysical and metal binding properties of **14a** and **14b** were compared with those of the analogous model squaraine dyes **17a** and **17b**. Depending upon the chain length of the pendent oxyethylene groups, the squaraine molecular wires **14a** and **14b** showed specificity in the sensing of various alkali metal ions. Upon metal ion binding, the absorption and emission intensities of **14a** and **14b** are considerably enhanced. The changes in the intensity of fluorescence emission of **14a** and **14b** are more significant upon metal ion complexation whereas the model squaraine dyes **17a** and **17b** showed only marginal changes in their emission intensity. This can be attributed to the non-planar to planar conformational changes of the extensively conjugated squaraine molecular wires compared to the less conjugated model squaraine dyes.

CHAPTER 1

RECENT DEVELOPMENTS IN π-CONJUGATED CONDUCTING POLYMER RESEARCH: A BRIEF REVIEW

1.1. Introduction

The design and synthesis of various soluble and processable organic π-conjugated macromolecules have opened up several new avenues in the area of modern advanced material research. Organic conjugated polymers possess interesting electronic and optical properties due to their unique delocalized π-electron systems. These properties are being explored for practical applications in electronic and optoelectronic devices, such as rechargeable batteries, electroluminescent display devices, information storage systems, and in communication technology. The discovery that it is possible to control the electrical conductivity of conjugated polymers over the range from insulating to metallic has led to considerable research activities in the development of conducting polymers for technological applications. Research on conducting polymers has raised several fundamental and technological challenges which have been taken up with great enthusiasm by a diverse community of chemists, physicists, material scientists and theoreticians. The significance of this area of research, both fundamentally and technologically, is clear from the large volume of publications, reviews, research monographs and patents that appeared in the literature during the past two decades.[1-12]

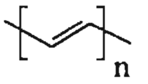
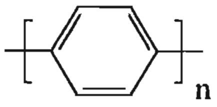
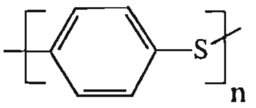
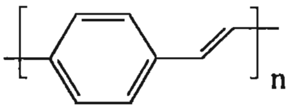
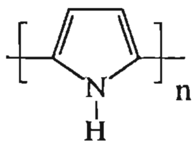
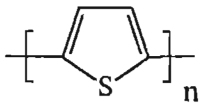
The key discovery in the area of conducting polymers was made in 1973 when it was reported that the inorganic polymer polysulfur nitride, $(SN)_x$ conducts electricity like a metal.[13] The room-temperature conductivity of $(SN)_x$ is of the order of 10^3 (Ω cm)$^{-1}$, to be compared with 6 x 10^5 (Ω cm)$^{-1}$ for copper and 10^{-14} (Ω cm)$^{-1}$ for polyethylene. The major breakthrough in the area of conducting polymers occurred in 1977 when Shirakawa *et al.* reported the conducting property of polyacetylene.[14] It was found that polyacetylene, which has an intrinsic conductivity much lower than 10^{-5} (Ω cm)$^{-1}$, could be made highly conducting, by exposing it to oxidizing or reducing agents.[15] Following this, several organic π-conjugated polymers have been synthesized and their optical and electronic properties have been evaluated. Polyanilines, polyphenylenes, polypyrroles and polythiophenes are a few well studied examples. The structures and conductivity values of some representative conducting polymers are listed in Table 1.

In recent years several advances have been made in conducting polymer research such as the efforts to synthesize low bandgap conducting polymers, self-acid-doped conducting polymers and π-conjugated polymer based sensors. The present review is intended to highlight the various strategies adopted for the synthesis of π-conjugated polymers, in particular, low bandgap, self-acid-doped conducting polymers and conjugated polymer based optical sensors. Prior to this, for a better understanding of the topic, a brief introduction to some of the basic aspects such as the theory and mechanism of conduction in π-conjugated polymers is given. In addition, the last part of this review is devoted for a brief introduction of squaraine dyes and their macromolecular analogues which are the central objects of the present investigation.

1.2. Electrical Conductivity of π -Conjugated Polymers

Electrical conductivity refers to the transport of charge carriers through a medium under the influence of an electric field or temperature gradient and is thus dependent on the number of charge carriers and their mobility. The charge carriers

Table 1. The structures and conductivity of doped conjugated polymers

Polymer	Structure	Dopants	Conductivity $(\Omega\ \mathrm{cm})^{-1}$
Polyacetylene		AsF_5, I_2, Li, K	$500\text{-}1.5 \times 10^5$
Poly(*p*-phenylene)		AsF_5, Li, K	500
Poly(*p*-phenylene sulfide)		AsF_5	3-300
Poly(*p*-phenylene-vinylene)		AsF_5	1-1000
Polypyrrole		electrochemical	40-200
Polythiophene		electrochemical	10-100

may be generated intrinsically or from impurities, in which case they may be electrons, holes, or ions. Alternatively, electrons or holes can be injected electrochemically. There are two types of electrical conductions, ionic and electronic, both of which have been the focus of intense research. Ionic conduction in polymers is associated with polyelectrolytes, whereas electronic conduction is associated with π-conjugated polymers and is a relatively new phenomenon.

1.3. Band Theory of Solids

In order to have a better understanding of the conduction phenomenon in polymers it is appropriate to have a brief discussion about the basic principles of the band theory of solids. When a large number of atoms, as in the case of metals or semiconductors, are brought together in the crystalline state, the electronic energy levels mix so as to form bands, each band consisting of electronic states with continuous energy levels. This situation is analogous to the splitting of atomic energy levels as two atoms are brought together to form a molecule. This can be better explained by considering the formation of a stack of several ethylene molecules as illustrated in Figure 1. A single ethylene molecule consists of two sp^2-hybridized carbon atoms, each containing an unpaired electron in a *p*-orbital which overlap to form a pair of bonding and antibonding orbitals separated by certain energy difference. When a second ethylene molecule is allowed to stack directly above the first, two sets of molecular orbitals are formed that are separated by energy $2\ \delta$, where δ is the resonance or transfer integral. Similarly, if 'n' number of ethylene molecules are allowed to interact, 'n' electronic states from each of the π and π^* orbitals are formed. If the value of 'n' is very large, the energy states will be close enough to form a continuous band.

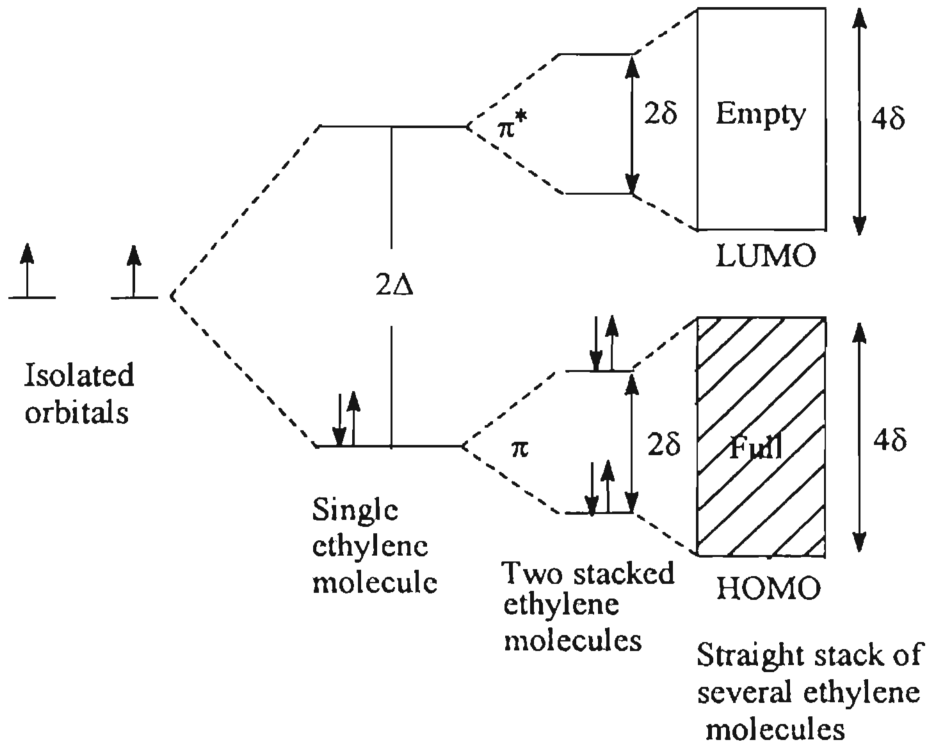


Figure 1. Evolution of band structure in ethylene molecules.

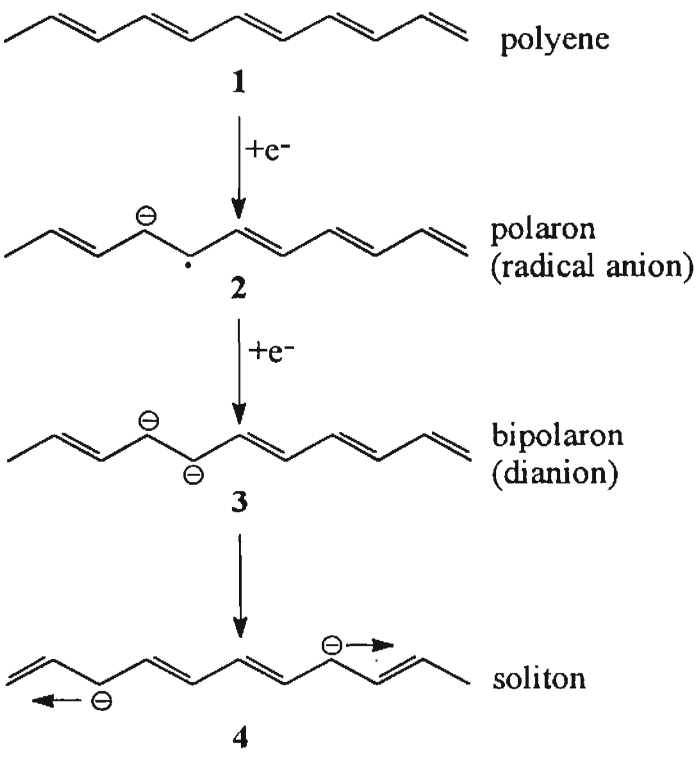
From Figure 1, it is clear that the band formed from the highest occupied molecular orbital (HOMO) in the stack of ethylene molecules is entirely full, whereas the band formed from the lowest unoccupied molecular orbital (LUMO) is entirely empty. The highest occupied electronic levels constitute the valence band (VB) and the lowest unoccupied levels, the conduction band (CB). The width of the forbidden band, or bandgap (Eg), between the VB and CB determines the intrinsic electrical properties of the material. In the case of the hypothetical stack of ethylene molecules, as shown in Figure 1, the HOMO (VB) band is completely filled. For the stack to be conductive, energy must be supplied to move an electron to the conduction band. In the case of insulators and semiconductors, this energy gap separating the two bands is high (>1.5 eV) whereas in the case of metals, the VB is only partially filled and the empty states which exist close to the Fermi level facilitate the conduction. Cowan and Wlygul have discussed this topic from the organic viewpoint within which chemists can appreciate the salient features of the theory.[16]

1.4. Conduction Mechanism. Polarons, Bipolarons and Solitons

The origin of the conduction mechanism has been a subject of controversy ever since conducting polymers were first discovered.[17,18] At first, doping was assumed to simply remove electrons from the top of the valence band (oxidation) or add electrons to the bottom of the conduction band (reduction). This one-electron model is associated with charge carriers having free spins (unpaired electrons). The measured conductivity in most cases is far greater than what can be accounted for on the basis of free spins alone. In order to account for this phenomenon of spinless conductivity, physicists have introduced the concept of transport via structural defects in the polymer chain.

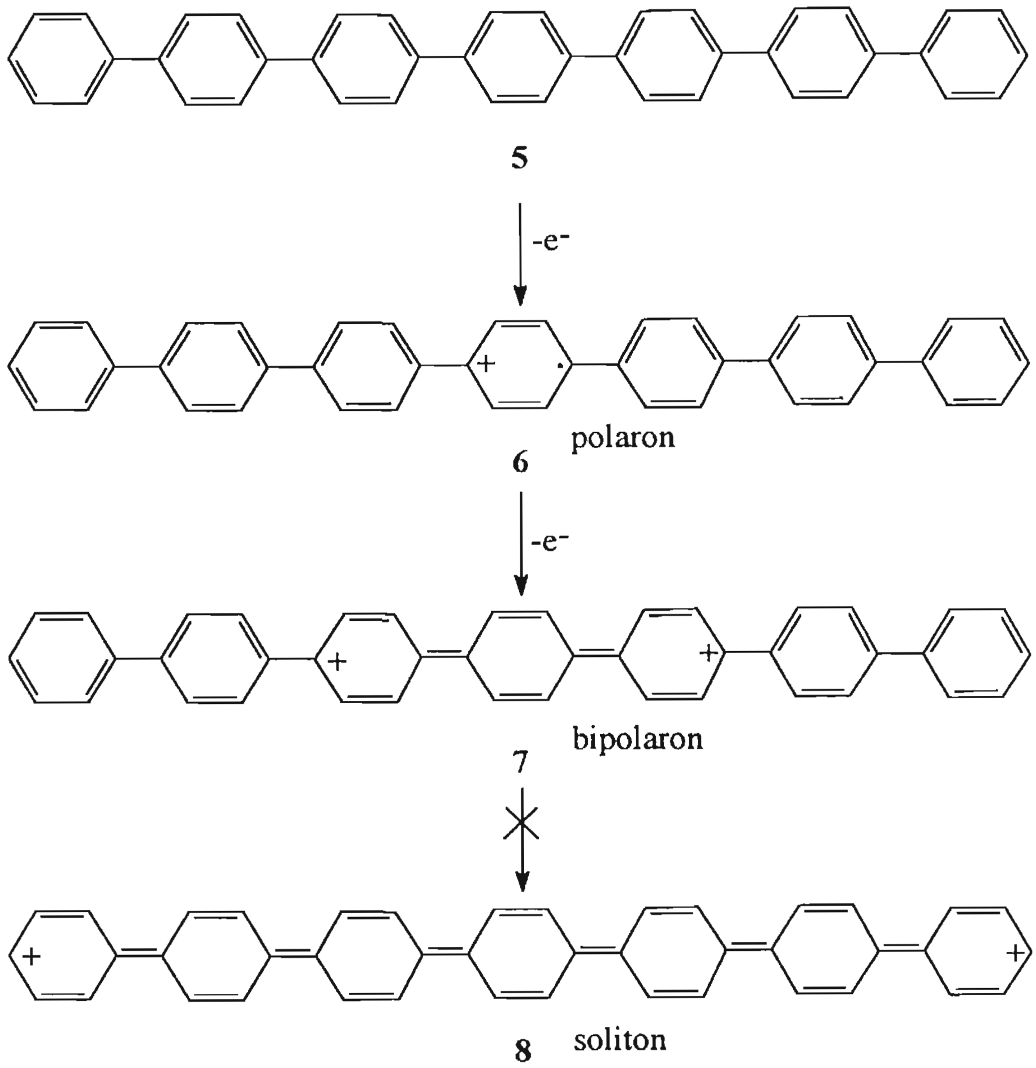
The reduction or oxidation process consists of adding or removing one electron to or from the polymer chain, which causes the injection of states from the top of the valence band and bottom of the conduction band into the energy gap. This electronic excitation in polymeric materials is accompanied by a distortion or relaxation of the lattice around the excitation, which minimizes the local lattice strain energy. The combined structural and electronic excitation will now look like a defect on the chain. From a chemical viewpoint, this defect is interpreted as a radical cation or radical anion, whereas Physicists refer to it as a polaron which carries both spin and charge.

Removal or addition of a second electron from or to a polaron results in the formation of a bipolaron. A bipolaron is thus identified as a dication or dianion associated with a strong local lattice distortion. In the case of polymers with degenerate ground state as in the case of polyacetylene, the charges can migrate apart to form solitons. This separation of the charges is possible because a polyene segment of equivalent energy is formed between the charges as they separate. The formation of polaron, bipolaron and soliton, in the case of a *trans*-polyacetylene can be represented as shown in Scheme 1.



Scheme 1. The reduction of trans-polyacetylene to form polaron, bipolaron and soliton.

In polymers with nondegenerate ground states, the mechanism is similar, but pairs of solitons cannot completely separate because polymer segments of higher energy would form between the charges. Thus, in the case of poly(*p*-phenylene), the formation of the less stable quinoid structure is less favourable and hence prefers the formation of bipolaron instead of soliton (Scheme 2). Electronic



Scheme 2. The oxidative doping of poly(*p*-phenylene). Bipolaron is the final oxidation product.

structures similar to that of poly(*p*-phenylene) are expected for most conducting polymers because a few have the degenerate ground states required for soliton formation. This has been experimentally proved in several conducting polymers such as poly(*p*-phenylene), polypyrrole and polythiophene.[19-21] A detailed treatment of the polaron, bipolaron and soliton formation in π-conjugated polymers, from the organic viewpoint has been made by Bredas and Street[22] and Tolbert.[23]

1.5. Doping of Organic Conjugated Polymers

As indicated earlier, most of the conjugated polymers have a completely filled valence band and an empty conduction band. The energy gap between VB and CB is usually high (>1.5 eV) so that the polymers are intrinsically insulating. Therefore, energy is to be supplied to remove electrons from the top of the VB or to add electrons to the bottom of the CB. This process is called doping. Conjugated polymers can be made conductive by doping which is carried out through chemical,[5] electrochemical[24] or photochemical[25] routes.

Doping can be either oxidative (p-doping) or reductive (n-doping). Therefore, doping agents or dopants are either strong oxidizing or strong reducing agents. Doping can be represented by the following simplified steps.

$$\text{(i) Polymer} + \text{Dopant} \xrightarrow[\text{p-type}]{\text{oxidation}} (\text{Doped polymer})^{+} + \text{Dopant}^{-}$$

$$\text{(ii) Polymer} + \text{Dopant} \xrightarrow[\text{n-type}]{\text{reduction}} (\text{Doped polymer})^{-} + \text{Dopant}^{+}$$

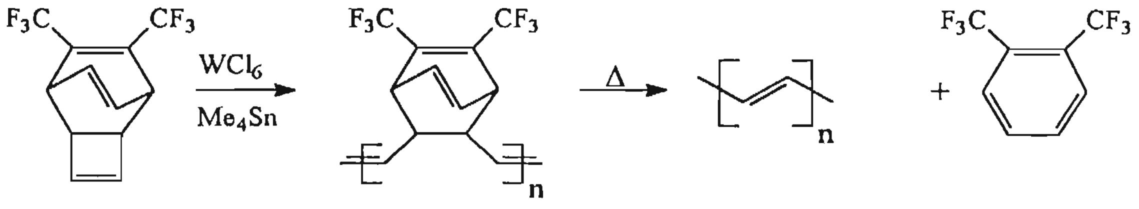
Dopants can be inorganic neutral compounds, ionic salts, organic compounds or even polymeric electrolytes. On doping, ionic states of the polymer (polarons or bipolarons) may be delocalized along the polymer backbone which will be neutralized by the counterion derived from the dopant. Since conjugated polymers possess potential redox sites, they can be doped to generate relatively high density of charge carriers. The bonding leads to the delocalization and transport of electrons along the polymer chains, thereby increasing the charge carrier mobility. This also facilitates the three dimensional transport of charge carriers by inter chain electron hopping.[26] The conductivity of the doped material can be varied and controlled by the amount of dopant used. Polymers such as polyacetylene, polyphenylene, polyphenylene sulfide, polypyrrole, polythiophene and polyaniline can be doped either by chemical or electrochemical methods to achieve conductivity in the range of 1 to 2000 S/cm.[27-34]

1.6. General Methods of Preparation of Conducting Polymers

Recent developments in the field of organic chemistry have led to the synthesis of several novel conducting polymers. Even though chemical methods are widely employed for the synthesis of soluble and processable conducting polymers, electrochemical and photochemical pathways are also used in several cases.

1.6.1. Chemical Routes

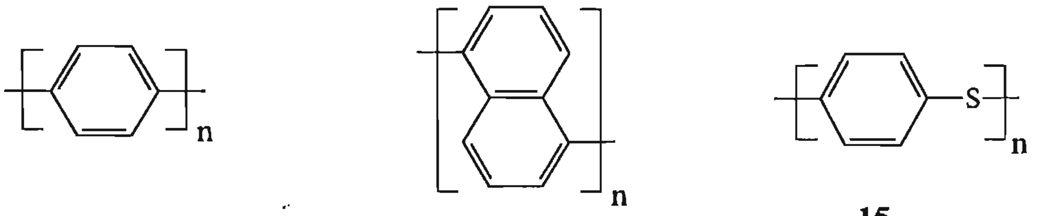
Polyacetylene, the first organic conducting polymer discovered, can be synthesized by a variety of chemical routes. The most widely pursued route is *via* the Zeigler-Natta polymerization of acetylene.[35] Since, polyacetylene obtained by this method is insoluble and difficult to process, a soluble precursor route has been developed, which on thermal elimination yield the required polymer.[36,37] A typical example is shown in Scheme 3.



9 **10** **11** **12**

Scheme 3

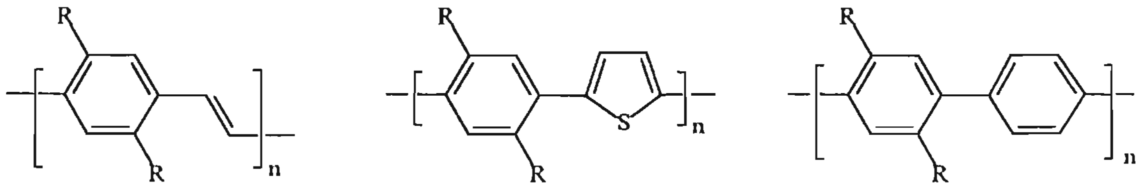
Poly(*p*-phenylene) (**13**) and polynaphthalene (**14**) are prepared from benzene and naphthalene respectively, in arsenic trifluoride solvent using AsF_5 catalyst [38,39] whereas poly(phenylene sulfide) (**15**) is obtained by the condensation of *p*-dichlorobenzene with sodium sulfide (Chart 1).[40] Poly(*p*-phenylene) can also be prepared by the reaction between *p*-dibromobenzene and magnesium in ether in the presence of nickel chloride bipyridyl catalyst.[41] Recently, several sulfur and phosphorous containing polymers have been prepared and are reported to have electrical conductivity.[42-45]



13 **14** **15**

Chart 1

Aniline and heterocyclic monomers such as pyrrole and thiophene can be chemically polymerized through oxidative routes using $(NH_4)_2S_2O_8$ or $FeCl_3$.[46-52] Polypyrrole and polythiophene have also been synthesized via Ullman coupling of the corresponding dihalides with copper powder.[53,54] Palladium-catalyzed reactions have been extensively used for the synthesis of conjugated polymers. For example, the Heck reaction was successfully utilized to synthesize poly(phenylenevinylene) (PPV, **16**) and its derivatives.[55-59] Similarly, the Stille coupling reaction was employed to synthesize poly(phenylenethiophene) (PPT, **17**)[60,61] and the Suzuki reaction was explored to synthesize poly(*p*-phenylene) (PPP, **18**).[62-65] The main advantage of these reactions is that they can be carried out under mild reaction conditions and can tolerate many functional groups. Stille coupling has also been used for the synthesis of well defined oligo- and poly(pyrrole-2,5-diyl). [66-71] A transition-metal catalyzed route to 100%, 1,4-linked poly(*p*-phenylene) (PPP) through a soluble precursor route has been developed by Gin *et al.*[72] This method offers the possibility of obtaining processable PPP which are otherwise insoluble and infusible and hence difficult to process.



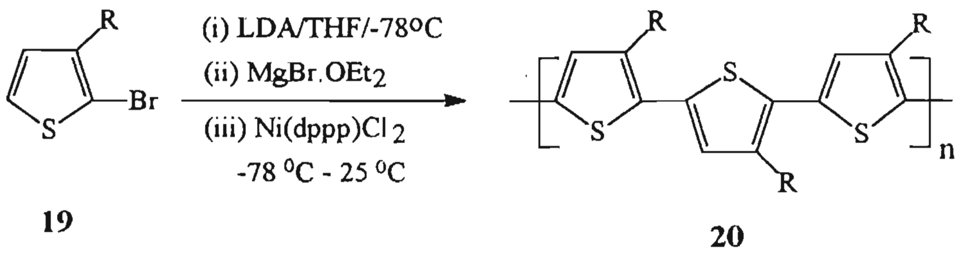
PPV
16

PPT
17

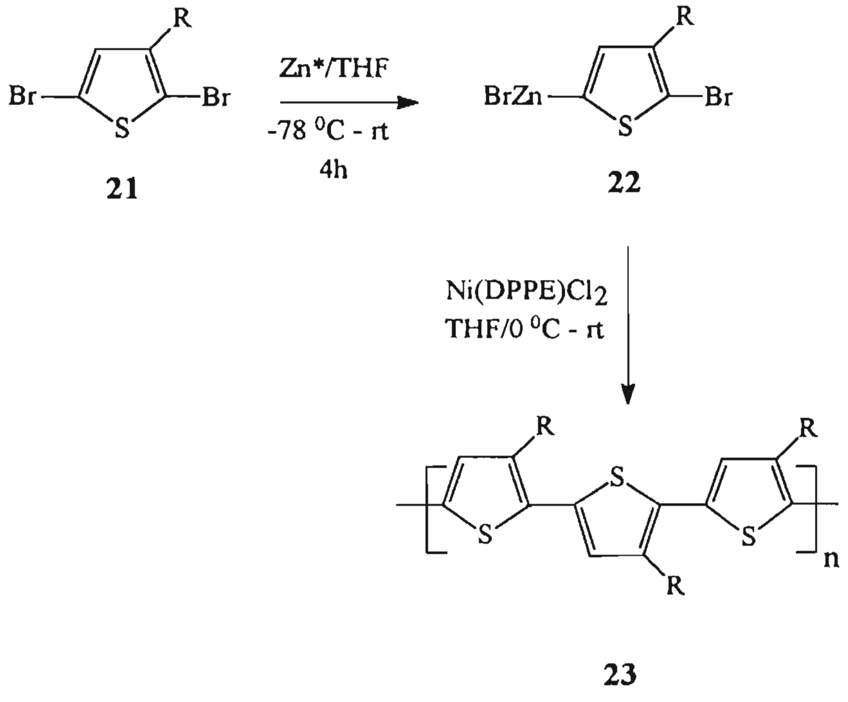
PPP
18

Chart 2

Regiocontrolled synthesis of poly(3-alkylthiophenes) using organometallic reagents has attracted a great deal of attention due to their improved electronic and optical properties. Progress toward these goals has led to the synthesis of structurally homogeneous, head-to-tail (HT) coupled polythiophenes (Scheme 4).[72-77] A systematically regiocontrolled synthesis of poly(3-alkylthiophenes (P3AT) mediated by Rieke zinc has also been reported (Scheme 5).[78-81]

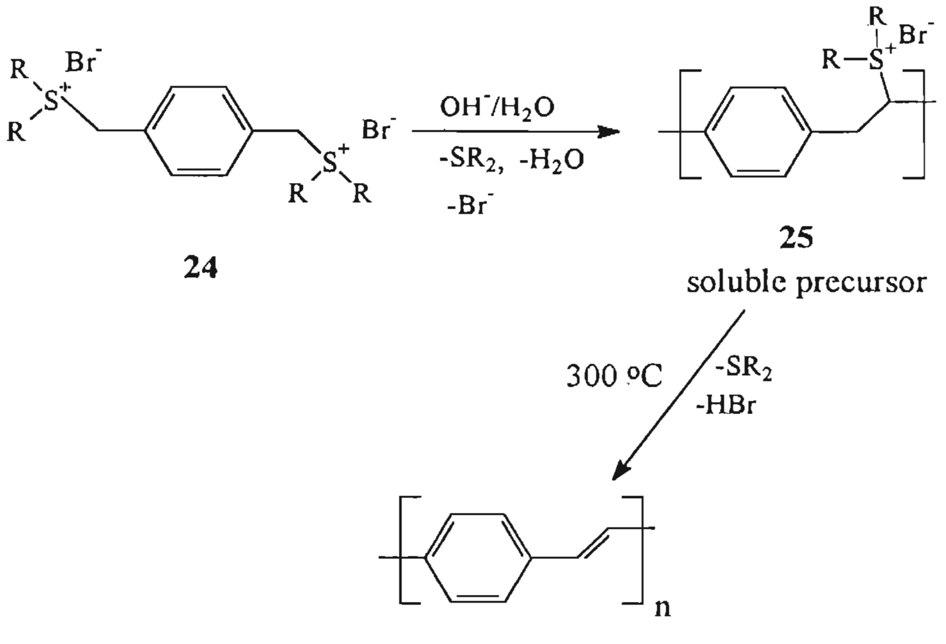


Scheme 4



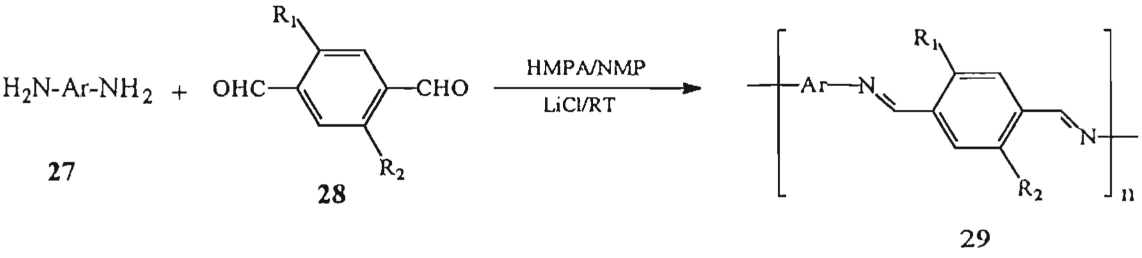
Scheme 5

Synthesis of poly(1,4-phenylenevinylene) (PPV) and its derivatives has attracted much attention due to its significance in electro-optical devices and molecular electronics. These polymers can be readily prepared in high molecular weights through the water soluble precursor route (Scheme 6).[82-87] In addition, synthesis and properties of several interesting, unconventional extended π-conjugated systems have been reported in the literature.[88]



Scheme 6

A simple and novel synthetic route to conjugated polymers are the polycondensation of aromatic diamines with aromatic diketones or dialdehydes to form polyimines (polyazomethines) as shown in Scheme 7.[89,90] A polycondensation route towards conjugated polymers would be a desirable synthetic alternative in order to allow a wider variety of monomers to participate and also to give a cleaner, better defined polymer than the nondiscriminating oxidative polymerization.



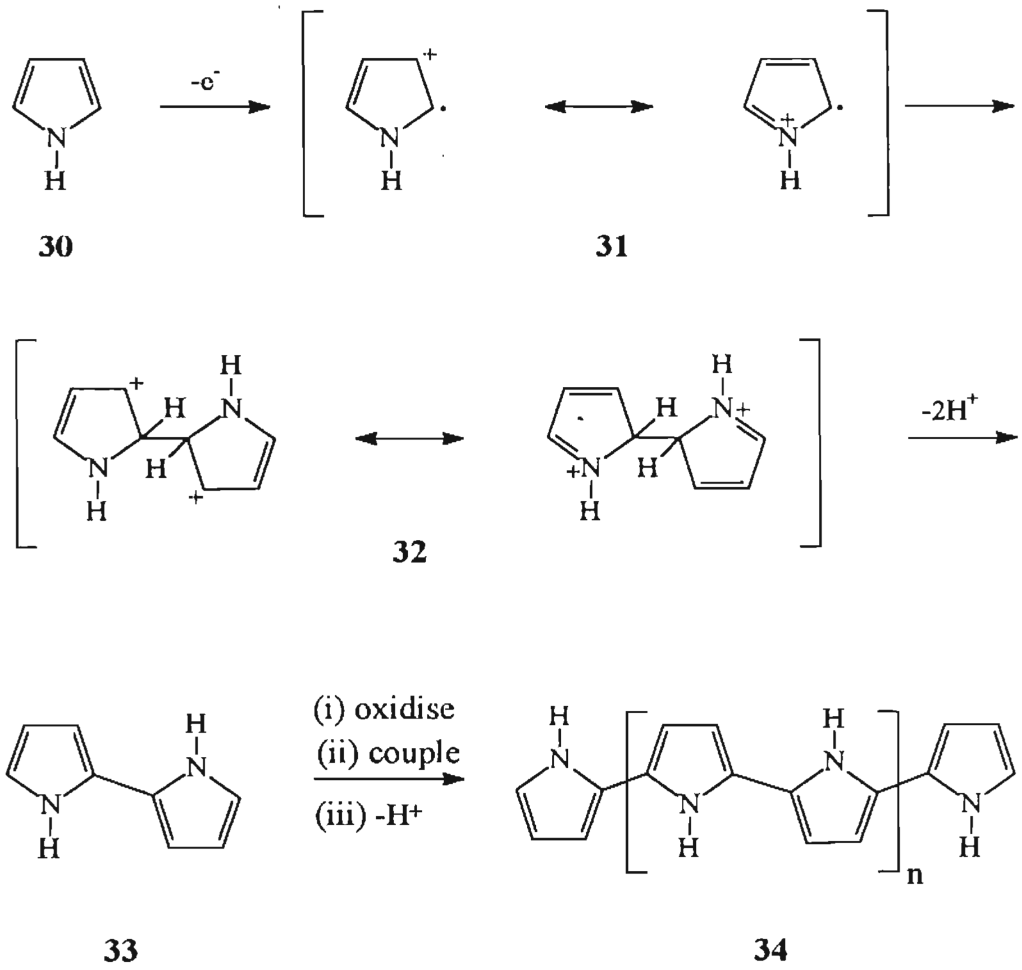
27 28 29

Scheme 7

1.6.2. Electrochemical Synthesis

Electrochemical oxidation of resonance-stabilized aromatic molecules has emerged as a viable method for the preparation of doped conducting polymer films. Thus, the electrochemical oxidation of pyrrole at a platinum electrode in the presence of a supporting electrolyte produces a free-standing electrically conducting polypyrrole film.[91,92] Several other aromatic monomers such as thiophene[93-96], carbazole[97], azulene[93,98], indole[93], aniline[99-102], phenol[103], thiophenol[104], bithiophene[105], 3-substituted thiophenes [106,107] and pyrene [108,109] have been similarly electropolymerized. All the resultant polymers have a conjugated backbone and are oxidized electrochemically as they are formed on the electrode from a solution containing both electrolyte and monomer. This oxidation leads to the incorporation of charge compensating anions onto the oxidized film and therefore the polymer films are in the doped conducting form.

Several studies of the electropolymerization of pyrrole and thiophene onto a number of supporting electrode substrates have been made in an attempt to elucidate the mechanistic details of the initial stages of polymerization and the effect of reaction conditions on polymerization. Based on these studies the mechanism for the electropolymerization of pyrrole can be depicted as shown in Scheme 8. A major advantage of electrochemical polymerization over the standard

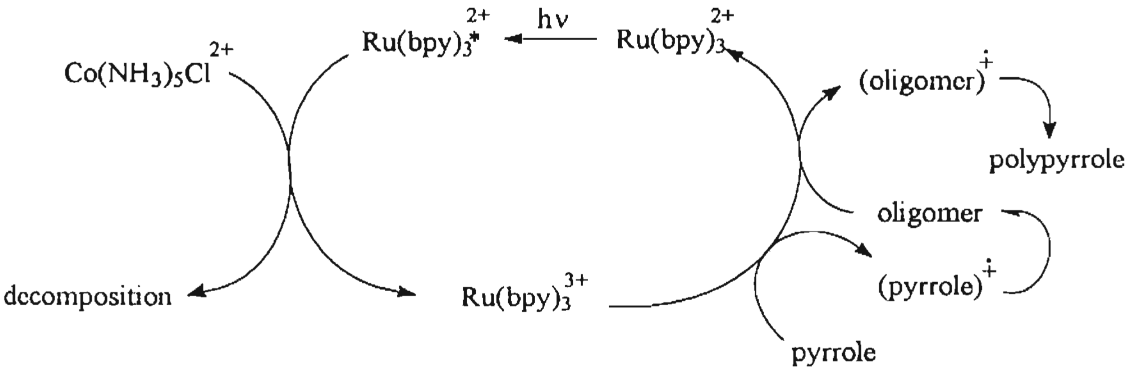


Scheme 8

chemical methods for the preparation of conducting polymers is the *insitu* formation of the doped polymer which gets directly coated as a film onto the electrode surface. Free standing polymer films can also be made by this method.

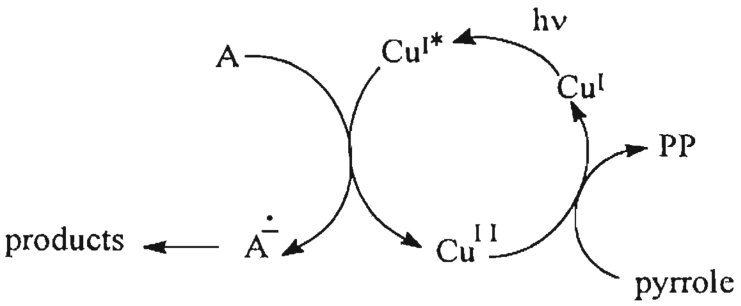
1.6.3. Photochemical Synthesis

Unlike the chemical and electrochemical routes, photochemical methods for the preparation of conducting polymers are not very common. However, there are a few scattered reports pertaining to the photochemical polymerization of pyrrole and some thiophene derivatives. A novel photosensitized polymerization of pyrrole has been reported using tris(2,2'-bipyridine)ruthenium (II) as the photosensitizer in aqueous medium (Scheme 9).[110]



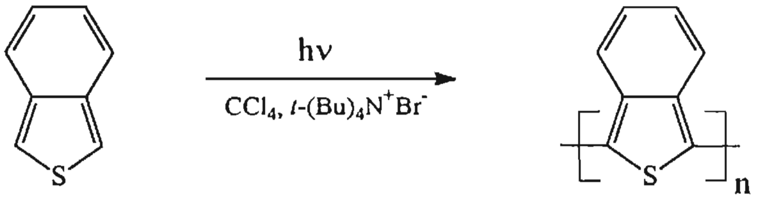
Scheme 9

Photochemical deposition of polypyrrole on to any type of solid surface can be achieved by the visible light irradiation of a solution of pyrrole in the presence of $Cu^{I}(dpp)^{2+}$ as the electron donor and *p*-nitrobenzyl bromide as the electron acceptor (Scheme 10). Irradiation of benzo(c)thiophene (**35**) in CH_3CN in the presence of CCl_4 and tetrabutylammonium bromide has resulted in the formation of poly benzo(c)thiophene **36** (Scheme 11).[112] In a recent communication Catellani *et al.* have reported the photochemical polymerization of dithieno[3,4-b; 3'-4'-d]thiophene (**37**).[113] The advantage of photochemical route like electrochemical method is the possibility of obtaining thin optical quality films of the conducting polymers directly on any type of solid supports such as indium-tin oxide (ITO) plated glass.



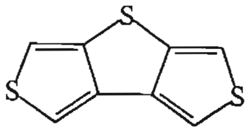
A = electron acceptor
Cu^{I}= Cu(dpp)$_2^+$
PP = doped polypyrrole

Scheme 10



35 **36**

Scheme 11



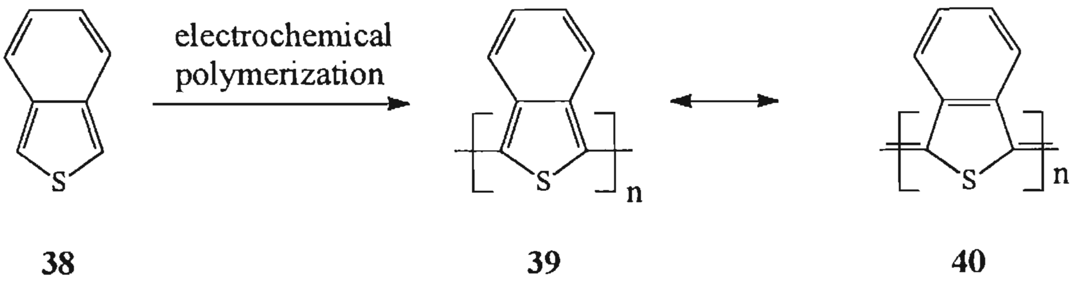
37

1.7. Low Bandgap Conducting Polymers

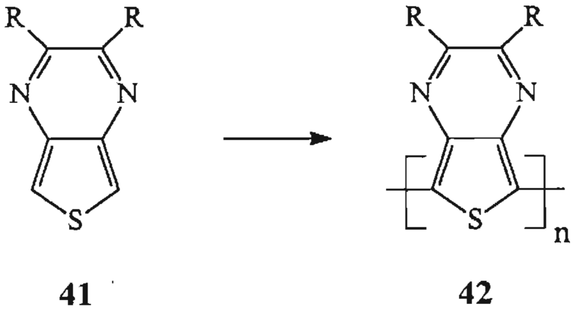
The design and synthesis of low bandgap (Eg) conjugated polymers is one of the major challenges in the area of polymers for electronic and optoelectronic applications.[114] Since, Eg governs the intrinsic electronic and optical properties of conjugated polymers, it constitutes the key to many fundamental and technological problems. The significance of low bandgap polymers is that, they show metal-like intrinsic electrical conductivity (without doping) and are good candidates for non-linear optical materials.

The possibility to synthesize low bandgap polymers was predicted based on several theoretical calculations and modelling.[115,116] In the theoretical design of small Eg polymers, the relative stability of structural isomers of a given polymer plays a vital role.[117] The combination of MNDO and Huckel molecular orbital methods provide a firm theoretical basis to the synthesis of low Eg conducting polymeric materials. Based on the theoretical calculations, two main strategies have been developed towards the design of low bandgap polymers. The first approach involves the tailoring of monomer structure in order to increase the quinoid character of the resulting π-conjugated system at the expense of its aromaticity. The important factors which determine the energy gap in such cases are the degree of coplanarity between adjacent repeat units and the relative amounts of their aromatic and quinoid character. Based on this principle, several small bandgap conducting polymers have been synthesized in recent years, majority of which are based on thiophene derivatives.

A classical example of a low bandgap polymer is polyisothianaphthene (PITN, **39**) which has been prepared by the electrochemical polymerization of isothianaphthene (Scheme 12).[118,119] Polyisothianaphthene can be considered as a polymer of a "nonclassical" thiophene and therefore exhibit higher stability than poly(thiophene) because of the resonance stabilization. This polymer is reported to have a bandgap of 1.1 eV which is nearly 1.0 eV below that of the parent



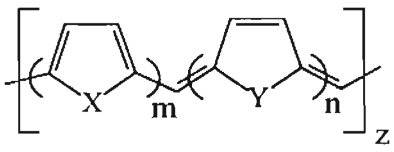
Scheme 12



Scheme 13

polythiophene (Eg = 2.1 eV). Incorporation of two nitrogen atoms in the aromatic ring at 4 and 7 positions yielded the pyrazino derivative (**41**) which has been predicted to have reduced steric interactions and hence a lower Eg (0.86 - 1.02 eV) (Scheme 13).[120,121]

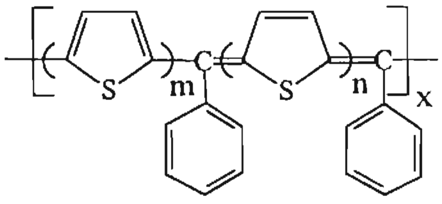
Another interesting class of low band gap polymers having alternate aromatic and quinoid subunits are shown in Chart 3. These methine-bridged polymers are predicted to have low Eg (1 eV) and possess intrinsic semi-conducting properties.[122-125] In a recent article, Hanack *et al.* have described the synthesis of several precursor molecules which are useful for designing of low bandgap polymers of the general structure **45** (Chart 4).[126]



43

X = O, S, NR, CH=CH

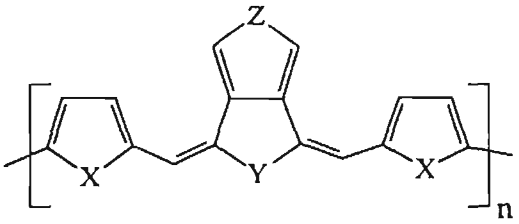
Y = O, S, SO, SO_2, NR, CH=CH



44

Chart 3

Electrochemical polymerization of the thiophene-derived monomers **46** and **47** has resulted in the formation of the corresponding low bandgap polymers having Eg. of ~ 1.7 and 0.9 eV respectively.[127-129] This small value for Eg was ascribed to a combination of lowered HOMO-LUMO separation stemming from the non-classical moiety and reduced steric interactions between adjacent rings.[131-133]



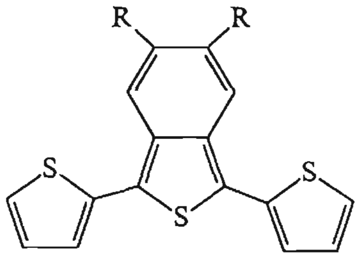
45

X = O, S, NR, CH=CH

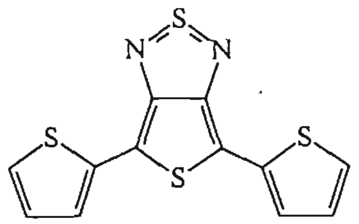
Y = O, S, SO, SO$_2$, NR, CH=CH

Z = S, CH=CH

Chart 4



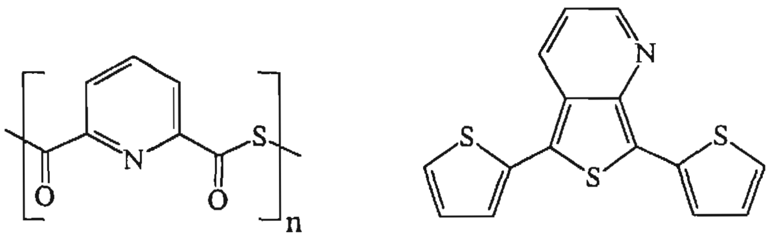
46



47

Chart 5

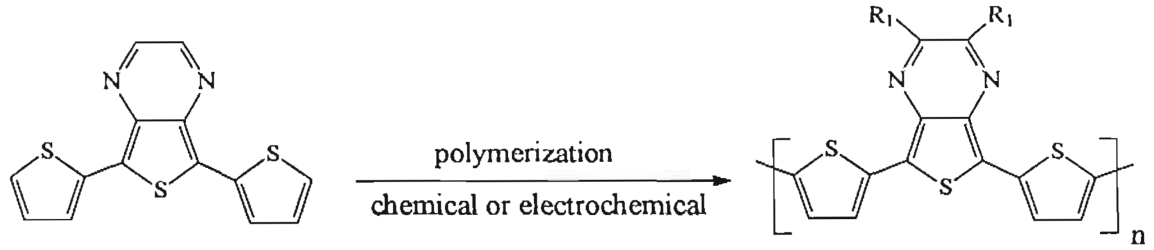
Incorporation of empty π-orbitals in the polymer chain by effective variation in the occupancy of frontier orbitals is another technique for the lowering of bandgap energy.[134] This has been illustrated in the case of poly(2,6-pyridinedicarbonyl sulfide) **48** which has an Eg of 0.85 eV. In another attempt Ferraris *et al.* have elucidated the relative contributions of steric and electronic effects on the value of Eg, by synthesizing a polymer from the monomer **49.** This polymer is reported to have a bandgap energy of 1.0 eV.[134]



48 **49**

Chart 6

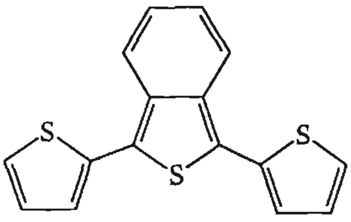
π-Conjugated polymers having alternate donor and acceptor groups are expected to possess low band gap energy due to the strong charge transfer interaction among the donor and acceptor groups. A representative example of such a system is **51** which consists of an aromatic donor (thiophene) and an *o*-quinoid acceptor (thieno[3,4-b]pyrazine) unit. The polymer **51** has been obtained from the corresponding monomer **50** by electrochemical or chemical polymerization routes (Scheme 14).[135]



50 **51**

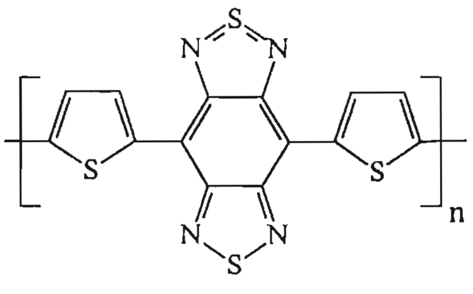
Scheme 14

In polymer **51**, when compared to the isoelectronic polymer **52**, there is no steric repulsion between the hydrogen atoms on the fused benzene ring and the adjacent thiophene rings. Therefore, polymer **51** is expected to have a coplanar structure resulting in an efficient π-electron delocalization along the main chain which has been experimentally proved from its physical data.

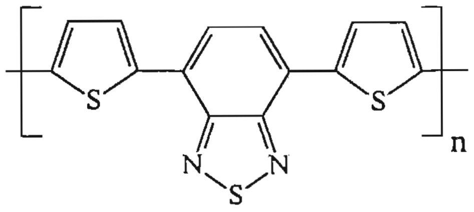


52

Recently Karikomi *et al.* have reported the synthesis of several interesting π-conjugated polymers having alternate donor acceptor groups.[137] Polymer **53** and **54** have low band gap energies due to strong charge transfer interaction between the thiophene and benzobis(1,2,5-thiadiazole) moieties (Chart 7). In these polymers thiophene is an aromatic donor and benzobis-(1,2,5-thiadiazole) is an *o*-quinoid type acceptor. These polymers are reported to have several distinct features and have low bandgap energies. The benzobis(thiadiazole) unit containing hypervalent sulfur atoms in **53** will exhibit high electron affinity.[138] Besides, the polymer **53** would be expected to be more stable due to appreciable contribution of its quinoid form **55**, containing the more stable classical 1,2,5-thiadiazole rings. Yet another advantage of **53** is that, this system has no steric repulsion between the adjacent heterocyclic units, and thereby leading to a planar geometry. Additionally, strong interchain interactions may be caused by short intermolecular S...N contacts which are often observed in 1,2,5-thiadiazole derivatives.[138-140]

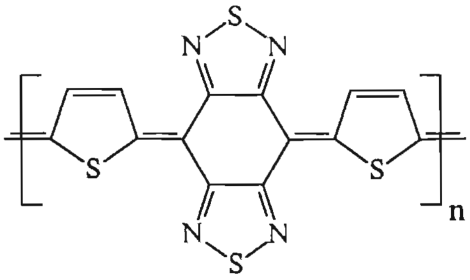


53



54

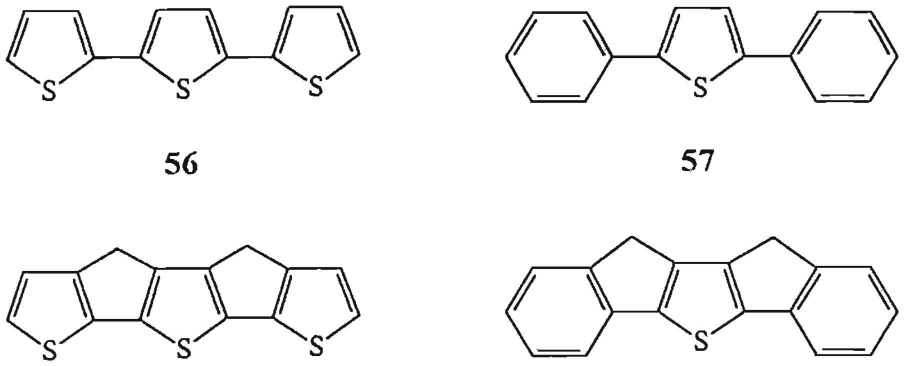
Chart 7



55

The bandgap energy of the polymer **53**, is estimated to be below 0.5 eV which could be the lowest value reported for an undoped π-conjugated polymer.[141] This extraordinarily low Eg value is due to the high electron affinity and large quinoid contribution of the benzobis(thiadiazole) ring. The rigid planar geometry with short S...N contacts may also contribute to the lowering of the bandgap. The electrical conductivity of the compressed pellets of undoped and I_2 doped polymers were 5 x 10^{-5} and 5.6 x 10^{-3} S/cm, respectively.

It has been reported that interannular rotations around single bonds severely limit the extension of effective conjugation in thiophene oligomers.[142-144] Based on this observation, Brisset *et al.* have shown that rigidification of a polythiophene backbone by the bridging of the thiophene rings allows a considerable reduction of the bandgap energy. Thus, rigid bithienyls exhibit significantly low bandgap energies than their non-rigid counterparts.[145,146] The validity of this strategy was tested by comparing the properties of the non-rigid compounds **56** and **57** with those of their rigid analogues **58** and **59** (Chart 8).[147] The electronic absorption spectra of **58** and **59** are bathochromically shifted from those of their respective monomers and showed fine structure typical of rigid conjugated systems. Thus, the Eg value of the rigid molecule **58** (1.65 eV) is nearly half of the value for the corresponding non-rigid compound **56** (3.2 eV).

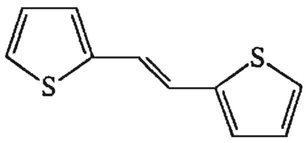


56 **57**

58 **59**

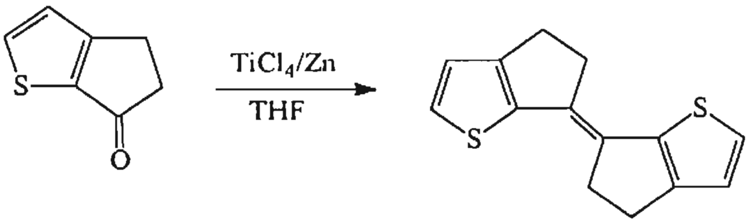
Chart 8

Poly(thienylenevinylene) (PTV) **60** has been shown to have small bandgap energy than polythiophene.[148] This has been attributed to the presence of double bonds of defined conformations which reduces the aromatic character of the π-conjugated backbone while limiting the number of possible rotations and hence the long-range deviation from planarity. In an attempt to further decrease the Eg value of **60**, Roncali *et al.* have synthesized **62**, a simplified model of **60**, by bridging the double bond and the thiophene ring.[149] This was achieved by the MacMurry dimerization of the cyclic ketone **61** using $TiCl_4$ and Zn (Scheme 15).



60

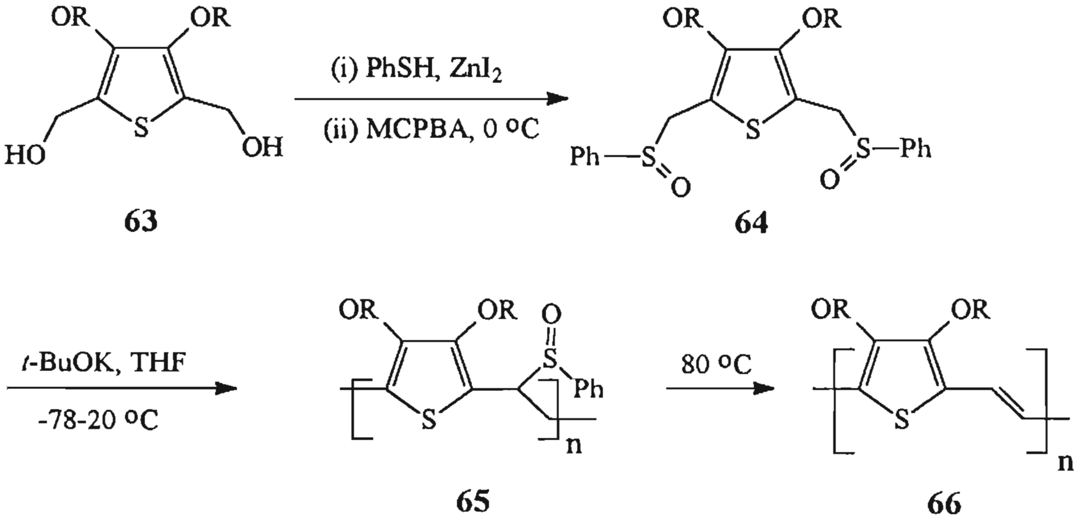
The optical absorption spectrum of **62** showed λ_{max} at 500 nm while the low energy absorption edge led to an estimated bandgap of 1.8 eV. The conductivity of this polymer was shown to be 10^{-2} S/cm by two-point probe method. Thus, the rigidification of dithienylethylene allows a considerable reduction in the Eg value and improvements in the electrochemical reversibility of the resulting conducting polymer. Conjugated oligomers having one dimensional graphite-like chains are also shown to possess low bandgap energies as in the case of polyperinaphthalene.[150-151]



61 **62**

Scheme 15

Synthesis of low bandgap conducting poly(3,4-dialkoxy-2,5-thienylene-vinylene) (**66**) has been reported recently by Cheng and Elsenbaumer.[152] Thus, for example, the bis(sulfoxomethylene) derivative **64** of dialkoxythiophene **63** afforded the conjugated polymer **66** *via* base, acid or thermally induced elimination of sulfoxide groups from the soluble precursor polymer **65** (Scheme 16). Unlike other methods, the sulfoxide precursor route afforded higher molecular weight polymers with longer effective conjugation length. The polymer **66** showed a deep blue colour (λ_{max} 680 nm) and a bandgap energy of 1.2 eV.



Scheme 16

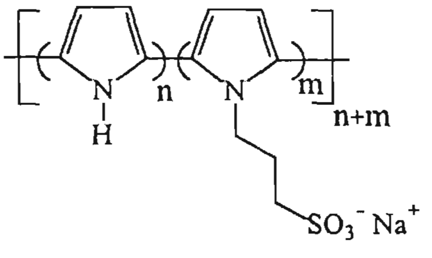
1.8. 'Self-Acid-Doped' Conducting Polymers

As mentioned earlier in this Chapter (Section 1.5), extended π-conjugated polymers can, in general, be transformed into conducting materials by doping.

Traditionally, doping is achieved by adding an external dopant. This kind of external doping process is often reversible and the counter ions or other neutralizing ions can move in and out many times. In addition to this, externally doped conjugated polymers are highly insoluble and intractable. In search of answers to such problems associated with conjugated polymers, Patil *et al.* have put forward the concept of 'self-acid-doped' conducting polymers.[153, 154]

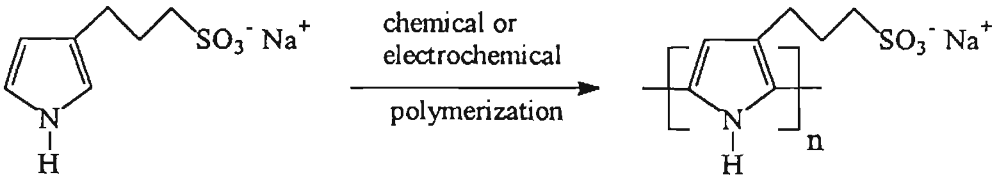
After the discovery of the self-doping phenomena, synthesis and properties of several 'self-acid-doped' conducting polymers have been reported. Sulfonic acid group functionalized pyrroles, thiophenes and anilines are the commonly employed monomers for this purpose. The bound ions in such monomers serve as internal dopants, thus causing the polymer to be 'self-doped'. The sulfonate species is chosen in view of its well known low reactivity in electrochemical redox processes. In this way, the ionic transport in the conducting polymer can be modulated by high density of anionic sites, thus requiring the cation to be the mobile species. In addition to this, the sulfonate group induces water solubility to the self-doped polymer.

The electroactive copolymer, **67** reported by Sundaresan *et al.* is shown to be self-doped due to the presence of covalently attached propane sulfonate moieties.[155] Detailed analysis of the electrochemical behaviour and cation



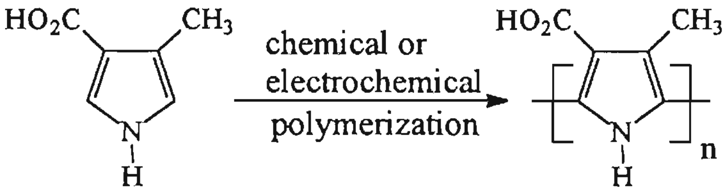
67

controlled charge transport parameters of this polymer have also been carried out. Following this report, Havinga *et. al.* have carried out detailed studies on the synthesis and properties of several 'self-acid-doped' conducting polymers of 3-substituted pyrroles (Scheme 17).[156,157] The polymer derived by the chemical or electrochemical polymerization of 3-methylpyrrole-4-carboxylic acid is also reported to be conducting without further doping (Scheme 18).[158]



68 **69**

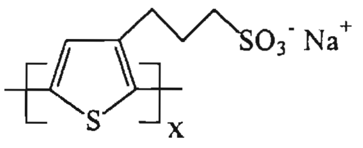
Scheme 17



68 **69**

Scheme 18

Several 'self-acid-doped' conducting polymers based on polythiophenes[159-165] and polyanilines[166,167] of the general structure **70** and **71** have been reported in the literature (Chart 9). The self-acid-doped polyaniline **71** is obtained by the direct sulfonation of the corresponding emaraldine base of polyaniline with fuming sulfuric acid. Alternative route to self- doped polyanilines is the direct reaction of their emeraldine or leucoemeraldine base with propane or butane sultone.[168-170]



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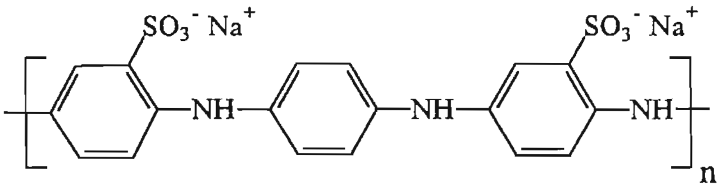
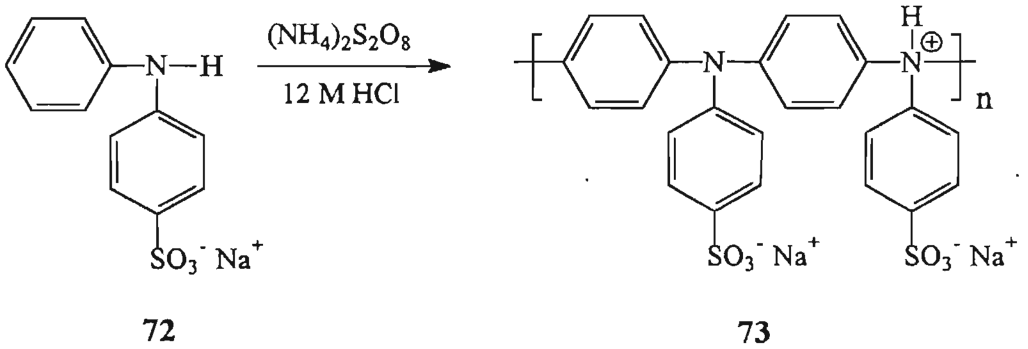


71

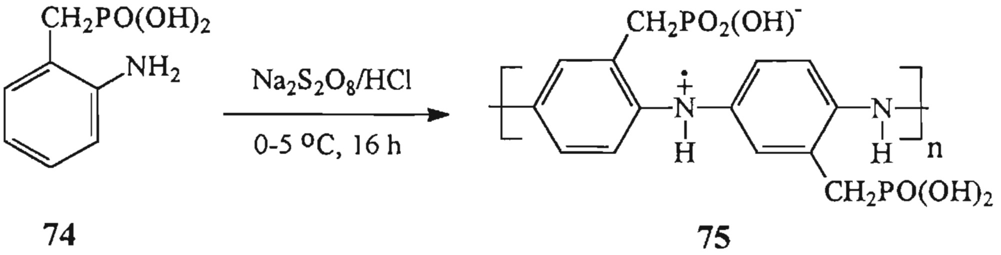
Chart 9

De Armitt *et al.* have reported the synthesis of a self doped polyaniline by the oxidative polymerization of the biphenylaniline sulfonic acid sodium salt (**72**) as per Scheme 19.[171] In a recent report, alkylphosphoric acid group has been used instead of SO_3H group, for the synthesis of a self-doped polyaniline.[172] Persulfate mediated oxidative coupling of *o*-aminobenzylphosphonic acid resulted in the formation of self-doped, water soluble polymers (Scheme 20).[173] This polymer is reported to have good redox stability and conductivity.

The covalent attachment of alkyl sulfonic acid or alkyl phosphoric acid groups to π-conjugated polymers not only induce self doping character to the polymers but also their water solubility and processability. In this way dopant ions become an integral part of the polymer back bone and is more compatible with the polymer. The environmental stability of the parent polymer is also enhanced by the presence of SO_3H groups. Moreover, the chemical, electrochemical, electrical and optical properties of self-doped polymers differ from those of their parent polymers.



Scheme 19



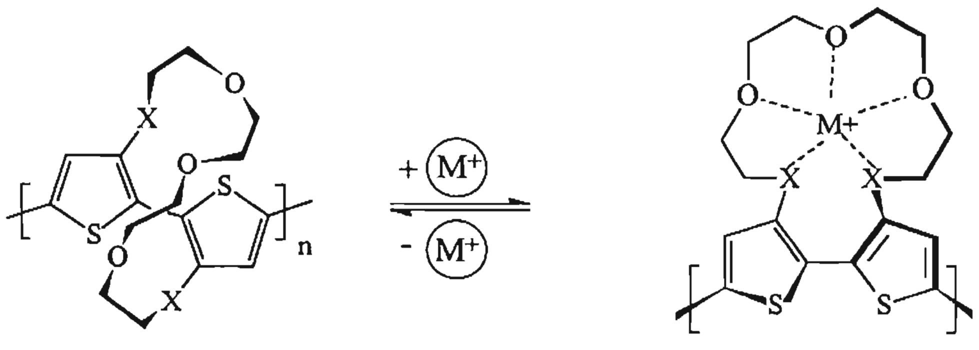
Scheme 20

1.9. Conjugated Polymer-Based Optical Sensors

The ensuing advances in the understanding and synthesis of conjugated polymers have opened up new paths towards the design and synthesis of several advanced materials. In this context, design and synthesis of molecular wires with tailored properties have assumed great significance. One can envisage several interesting applications of such materials in photovoltaic devices and molecular electronics.[174-177] Another interesting application of conjugated (conducting) polymers is their use as macromolecular sensors.

A molecule-based sensory device must efficiently transduce molecular interactions into readily measurable response. Such a device requires molecular recognition events occurring at receptors which have been designed in such way that different properties evolve from occupied and unoccupied states.[178] Representative examples of molecular sensory components are crown ether linked organic dyes in which optical changes associated with the molecular recognition events are exploited.[178]

Receptor-based conducting polymers are one class of materials that have been successfully utilized in the development of molecule-based sensory materials.[179-183] The reversible binding of an analyte by such a conducting polymer can produce perturbations in the chemical structure, oxidation state, and/or solid state ordering of the system resulting in voltammetric, ionochromic and chemoresistive responses. Conductivity or equivalent resistivity is the property which is most sensitive to a polymer's chemical or conformational changes. For example, it is well-known that twisting a conducting polymer's backbone from planarity can result in a conductivity drop as high as 10^5 S/cm or greater. Hence, conductivity changes in polymers provide a large dynamic range which, if harnessed effectively, can result in very sensitive sensory materials.[184-185] Toward this end, Marsella *et al.*[179,180] have designed several conducting polymer-based macromolecular sensors making use of the conformational changes of the polymer backbone, associated with a metal ion recognition a representative example of which is shown in Scheme 21.



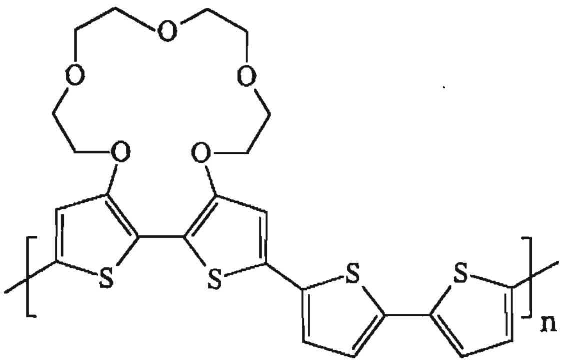
76 **77**

X= O or $-CH_2-CH_2-O-$

planar twisted

Scheme 21

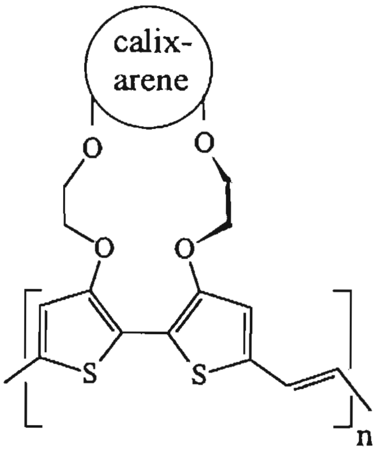
The polymers **76** and **78** upon binding with an appropriate metal ion, showed large shifts in their absorption maxima . Since, the optical spectral shift occurs in the visible region, a dramatic colour change could be noticed for these polymers. The large magnitude of the shift despite the low binding constants is ascribed to the additive effect of destroying conjugation at several points along a



78

highly conjugated system. This is supported by the fact that the polymer **78**, in which the number of twisting sites has been reduced, shows a smaller shift than the polymer **76**.

In an effort to further optimize the selectivity and sensitivity of conducting polymer based optical sensors, Marsella *et al.* have synthesized calix[4]arene-substituted polythiophenes **79** and **80** which show ion selective voltammetric, chromic, fluorescent and resistive responses. Although the sensory properties of these polymers are expressed *via* several measurable entities, the ionoresistive response is clearly the most sensitive.[186] The chemoresistive polymer **81** which is derived from the corresponding bithiophene containing cyclophane receptors, which are capable of forming self-assembled pseudorotaxane complexes with paraquat is an excellent example of a conjugated polymer based sensing material.[180,187]



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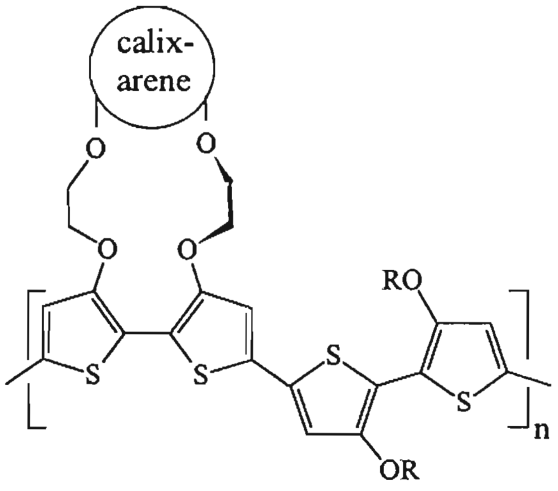
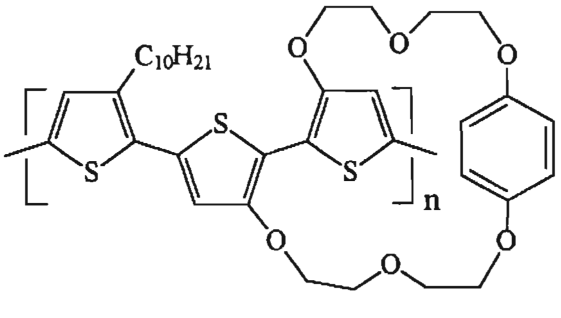


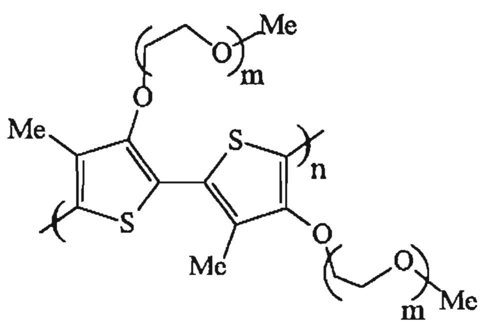
R = $-CH_2CH_2OCH_3$

80

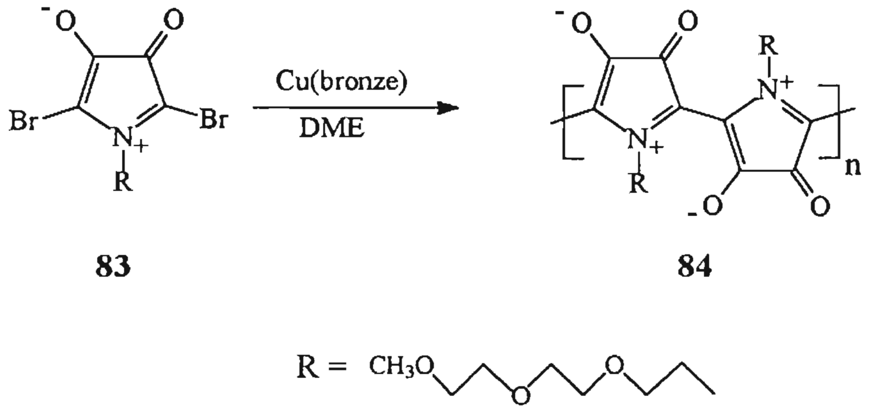


81

Levesque and Leclerc have synthesized an ionoselective polymeric sensor **82**, from oligo(oxyethylene) side-chain bearing thiophene derivative.[188] As observed in the case of several other regioregular poly(3-alkoxy-4-methylthiophene)s, poly(3-oligo(oxyethylene)-4-methylthiophene) **81** is thermo-chromic in both solid state and in solutions. The chromic effect of the polymer **81** is further influenced by addition of metal ions. A planar/non-planar conformational transition of the polymer is responsible for the thermo- and ionochromic effects of the polymer **81** .The low bandgap zwitterionic polymeric sensor **84** reported by Brockmann and Tour shows several interesting properties. This polymer which is prepared from the corresponding pyrrole derivative **83** not only responds reversibly toward Brownsted and Lewis bases but also is water soluble and optically sensitive toward addition of specific salts. The presence of oligoethylene substituents is critical for the dramatic ionochromic response of this polymer.



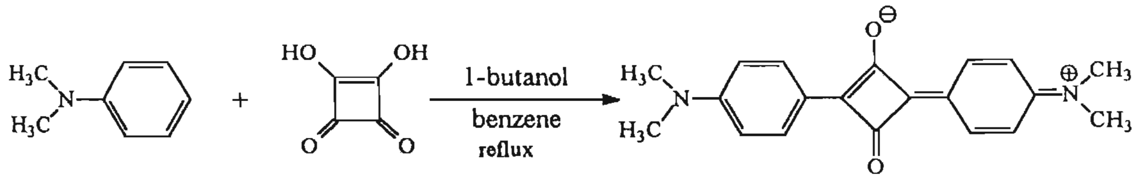
82



Scheme 22

1.10. Squaraines and Polysquaraines

3,4-Dihydroxy-3-cyclobutene-1,2-dione (squaric acid) is known to condense with electron rich aromatic and heterocyclic molecules such as N,N-dialkylanilines, phenols, pyrroles, and benzothiazoles to form highly coloured polar zwitterionic (betaine) dyes (Scheme 23).[191-195] Even though these dyes are known under various names, Schmidt proposed the name squaraines, which is now the most widely accepted nomenclature.[196] This class of organic dyes exhibits sharp and intense absorption in the visible region in solution. In the solid state, due to the extensive intermolecular charge-transfer interactions, the absorption becomes very broad with bathochromic shift to near IR region (panchromatic shift). These optical characteristics have made squaraines very attractive materials for a variety of industrial applications such as xerographic photoreceptors[197,198] organic solar cells,[199,200] and optical recording.[201]

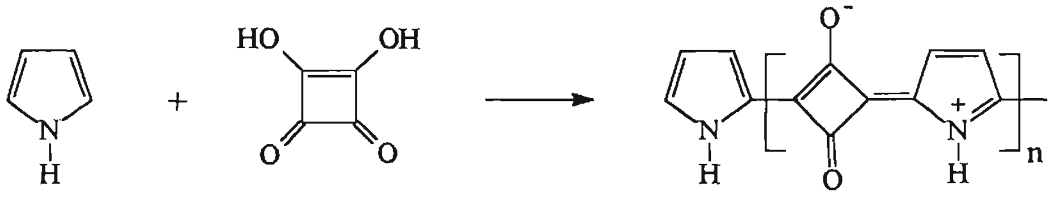


85 **86** **87**

Scheme 23

The major part of the earlier work on the synthesis of squaraines was carried out by Treibs and Jacobs and by Sprenger and Ziegenbein. Later, the pioneering work of Law has made significant contributions to squaraine chemistry, particularly to their synthesis and photoconducting properties.[202] Recently, Das and co-workers have added more information to the photophysical behaviour of a few representative squaraines.[203-208] Even though, the chemistry and properties of squaraines are well studied, there are not many reports pertaining to their macromolecular analogues.

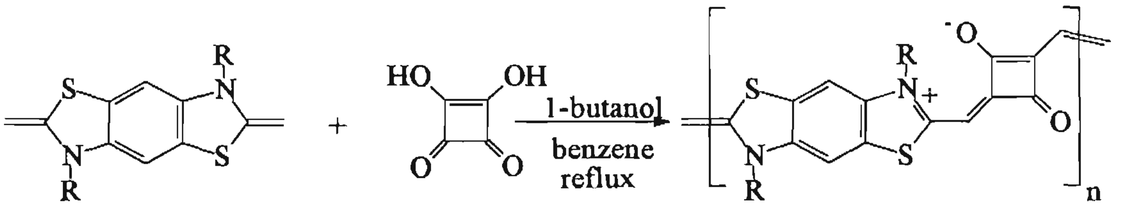
The earliest attempt to make a polysquaraine was made by Triebs and Jacob in 1965.[209] They found that condensation of pyrrole and squaric acid resulted in the formation of a dark blue insoluble material (Scheme 24). These authors have pointed out that the material **89** may have a low molecular weight (n = 2 or 3)



88 **86** **89**

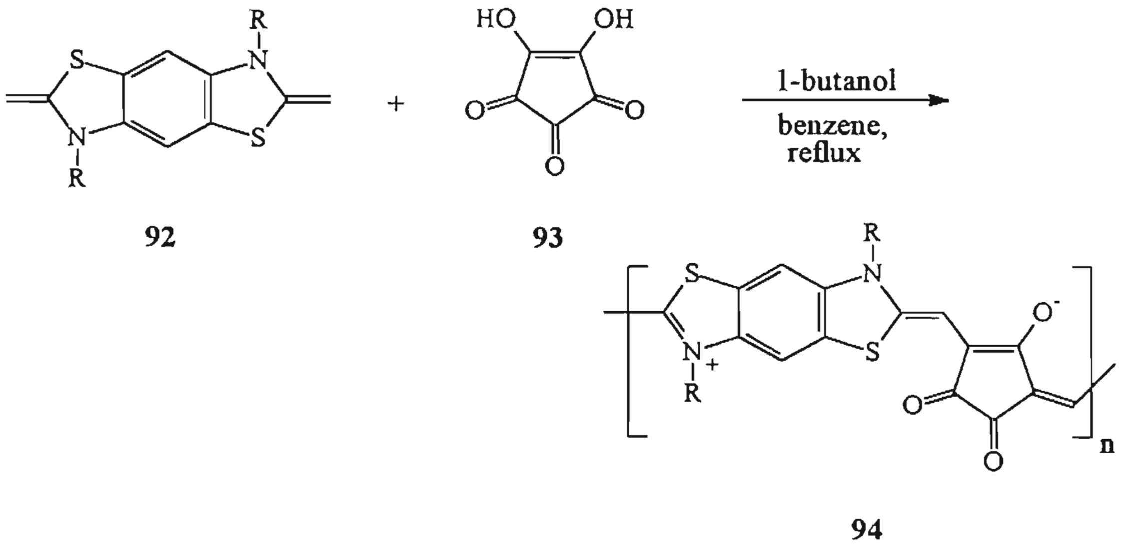
Scheme 24

and is highly insoluble and intractable under any conditions. Therefore, the actual structural constitution and properties of this material were unknown. Later, in 1992, Havinga *et al.* have synthesized a new class of polysquaraines and polycroconaines by the condensation of benzobisthiazoles with squaric acid and croconic acid, respestively.[210,211] (Schemes 25 and 26). These polymers were



90 86 91

Scheme 25

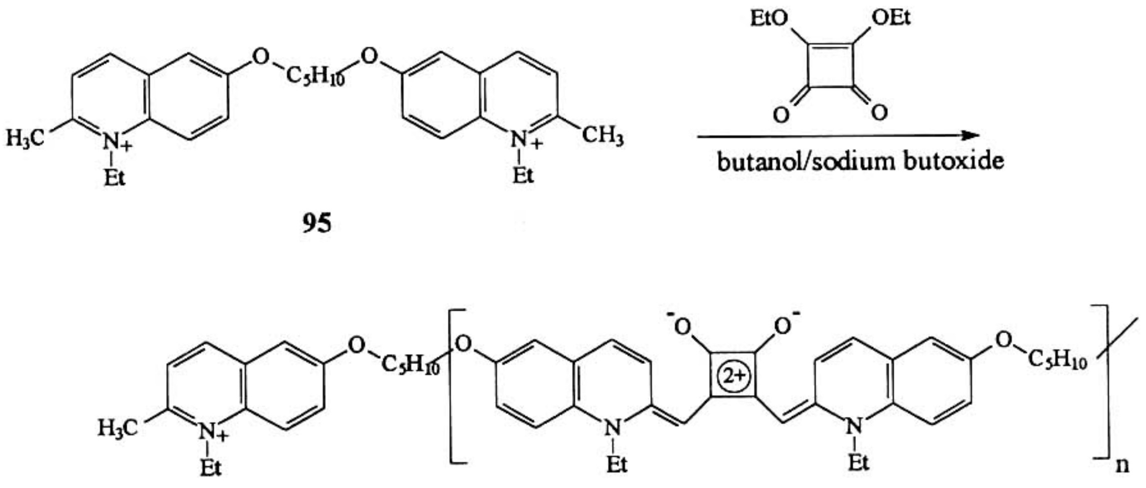


Scheme 26

observed to have small bandgap energies, down to 0.5 eV, upon doping with iodine. This low bandgap energy arises from the regular alternation of strong electron donor and acceptor moieties in the conjugated polymer backbone.

The reaction of diethyl squarate with a quinolidine bis-quaternary salt **95** was employed to prepare a polymer containing the repeating units of squaraines and long alkyl chains (Scheme 27)[212]. However, this polymer is not a through conjugated system and it has been prepared for testing its NLO activity.

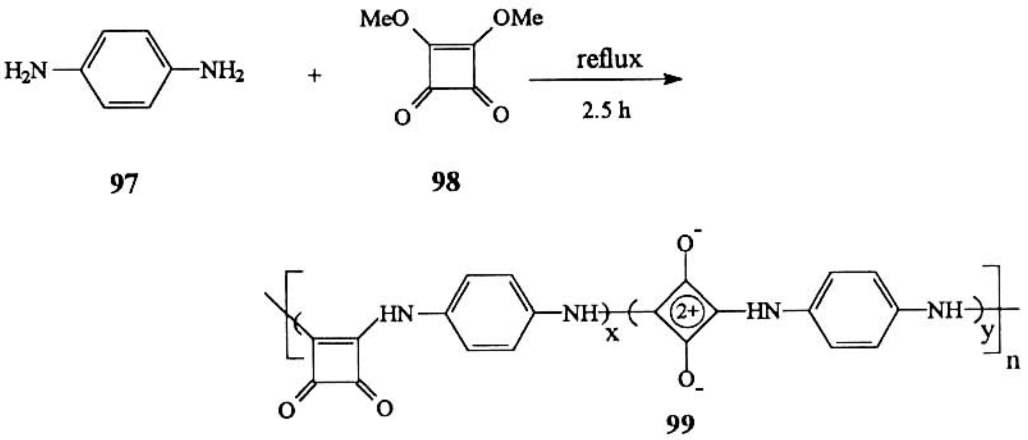
Condensation of squaric acid with aromatic primary diamine such as *p*-phenylene diamine is known to form polyamides of squaric acid. [213-218] Neuse and Green have carried out extensive studies on the synthesis of polyamides of squaryl esters and dianilines and found that the polymeric chains are composed of both the 1,2- and 1,3-oriented cyclobutenone repeat units (Scheme 28).[219-221] However, these condensation reactions are different from the usual squaraine dye formation and hence the products do not have any properties of the squaraine dyes.



95

96

Scheme 27



97

98

99

Scheme 28

The significance of squaraines in designing low bandgap conducting polymers is now attracting the attention of both experimental and theoretical chemists. Systematic theoretical studies by Brocks and Tol using *ab initio* calculations have predicted the factors that control the size of the bandgap energies in this class of polymers.[222,223] Car-Parrinello techniques have been used to optimize both the electronic and the geometrical structures of several possible polysquaraines and have arrived at the conclusions that bandgap energies ranging from 2.3 to as low as 0.3 eV can be achieved by choosing appropriate polymer repeat units. Thus, polysquaraines would be ideal for designing novel materials such as intrinsically conducting polymers, NLO active polymers and macromolecular optical sensors.

1.11. Conclusions

The brief survey of the literature on recent developments in conducting polymer research presented here reveals that tremendous efforts have been made in recent years in the design of novel π-conjugated polymers with improved properties. However, synthesis of such polymers and their starting monomers require multistep synthetic procedures. In most cases, problems associated with the solubility and processing restrict their technological applications. Therefore, simple and efficient synthetic approaches towards the synthesis of soluble π-conjugated polymers with properties such as low bandgap, good optical and electrochemical responses have great significance from both fundamental and technological point of view. In this context, the use of organic dyes having low HOMO-LUMO separation and excellent optical properties have great potential in designing soluble low bandgap polymers, 'self-doped' conducting polymers and macromolecular optical sensors. In the present thesis, these three important aspects have been addressed with respect to a new class of organic dye derived π-conjugated macromolecular systems namely polysquaraines.

1.12. References

1. Proceedings of the Workshop on Synthetic Metals, *Synth. Met.* **1984**, *9*, 129.
2. Proceedings of the International Conference on Synthetic Metals, *Mol Cryst. Liq. Cryst.* **1985**, 117.
3. Baker, G. L. in *Electronic and Photonic Applications of Polymers*, Bowden, M. J.; Turner, R. S. (Eds.), ACS, Washington, DC, **1988**.
4. *Handbook of Conducting Polymers*: Skotheim, T. J., Ed.; Dekker: New York, **1986**.
5. Bigg, D. M.; Bradbury, E. J. in *Conductive Polymers*; Seymour., Ed.; Plenum: New York, **1981**, pp 39-47.
6. Roth, S. in *Science and Application of Conducting Polymers*, Salaneck, W. R.; Clark, D. T.; Samuelson, E. J.; Eds.;Adam Hilger, Bristol, England, **1991**.
7. Heeger, A. J. in *Science and Application of Conducting Polymers*; Salaneck, W. R.; Clark, D. T.; Samuleson, E. J.; Eds.; Adam Hilger, Bristol, England, **1991**.
8. Mac Diarmid, A. G. in *Conjugated Polymers and Related Materials*; Salaneck, W. R.; Lundstorm I.; Ramby, R., Eds., Oxford Science Publication, **1993**.
9. Aldissi, M., Ed. *Intrinsically Conducting Polymers: An Emerging Technology*; Kluwer Academic Publishers: Dordrecht, The Netherlands, **1993**.
10. Bakshi, A. K. *Ind. J. Chem.* **1992**, *31A*, 291.
11. Miller, J. S. *Adv. Mater.* **1993**.
12. Maiti, S. *Ind. J. Chem.* **1994**, *33A*, 524.

13. Walatka, V. V.; Labes, M. M.; Perlstein, J. H. *Phys. Rev. Lett.* **1973**, *31*, 1139.
14. Shirakawa, H.; Louis, E. J.; Mac Diarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc. Chem. Commun.* **1977**, 578.
15. Chiang, C. K.; Fincher, C. R.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gau, S. C.; Mac Diarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098.
16. Cowan, D. O.; Wlygul, F. M. *Chem. Eng. News.* **1986**, *64 (29)*, 28.
17. Ehinger, K.; Roth, S. *Philos, Mag.* **1986**, *53*, 301.
18. Heeger, A. J. *Polym. J.* **1985**, *17*, 201.
19. Crecelins, G.; Stamm, M.; Fink, J.; Ritsoko, J. *J. Phys. Rev. Lett.* **1983**, *50*, 1498.
20. Scott, J. C.; Pfluger, P.; Krounbi, M. T.; Street, G. B. *Phys. Rev. B*, **1983**, *28*, 2140.
21. Chung, T. C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B.*, **1985**, *30*, 702.
22. Bredas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 309.
23. Tolbert, L. M. *Acc. Chem. Res.* **1992**, *25*, 561.
24. Diaz, A. F.; Rubinson, J. F.; Mark, H. B. *Adv. Polym. Sci.* **1988**, *84*, 113.
25. Crivello, J. V.; Lau, J. H. N. *Macromolecules*, **1977**, *10*, 1307.
26. Kivelson, S. *Phys. Rev.* **1982**, *B25*, 3798.
27. Chance, R. R.; Shacklette, L. W.; Miller, G. G.; Ivory, D. M.; Sowa, J. M.; Elsenbaumer, R. L.; Baughman, R. *J. Chem. Soc., Chem. Commun.* **1980**, 347.
28. Street, G. B.; Clark, T. C.; Krounbi, M.; Kanazawa, K.; Lee, V.; Pflunger, P.; Scott, J. C.; Weiser, G. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 253.

29. Dirk, C. W.; Inabe, T.; Schoch, K. F.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1539.

30. Orthmann, E. A.; Enkelmann, V.; Wegner, G. *Makromol. Chem. Rapid. Commun.* **1983**, *4*, 687.

31. MacDiarmid, A. J.; Chiang, J. C.; Ritchter, A. F.; Epstein, A. J. *Synth. Met.* **1987**,. *18*, 285.

32. Kim, O. K; *J. Polym. Sci. Polym. Lett.* **1982**, *20*, 663.

33. Nilbourn, K.; Murray, R. W. *Macromolecules*, **1988**, *21*, 89.

34. Basescu, N.; Liu, Z. X.; Moses, D.; Heeger, A. J.; Narman, H.; Theophilou, N. *Nature*, **1987**, *327*, 403.

35. Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem.* **1974**, *12*,11.

36. Edwards, J. H.; Feast, W. J. *Polymer*, **1980**, *21*, 595.

37. Edwards, J. H.; Feast, W. J.; Bott, D. C. *Polymer*, **1984**, *25*, 395.

38. Gibson, H. W. in *Handbook of conducting polymers*, Skotheim, T. A., Ed.; Dekker, New York, **1986**, pp 405.

39. Ehrlich, P.; Anderson, W. A. in *Handbook of conducting polymers*, Skotheim, T. A, Ed.; Dekker, New York, **1986**, pp 441.

40. Hill, H. W.; Brady, D. J. *Encyclopedia of Chemical Technology*, Kirk-Othmer, Ed., Wiley, New York, **1982**, *18*, 793.

41. Ikeda, Y.; Masaru, O.; Arakawa, T. *J. Chem. Soc. Chem. Commun.* **1983**, 1518.

42. Gutierrez, M. H.; Ford, W. T.; Poohl, H. A. *J. Polym. Sci.; Polym. Chem. Edn.* **1984**, *22*, 3789.

43. Rahman, M. S.; Mahapatra, M.; Maiti, M. M.; Maiti, S. *J. Polym. Mater.* **1989**, *6*, 135.

44. Mahapatra, M.; Rahman, M. S.; Maiti, M. M.; Maiti, S. *J. Polym. Mater.* **1989**, *6*, 213.

45. Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 9.

46. Chien, J.C.W.; Wnek, G. E.; Karasz, F. E.; Hirsch, J. A. *Macromolecules*, **1981**, *14*, 479.

47. Chiang, J.-C.; MacDiarmid, A. G. *Synth. Met.* **1986**, *13*, 193.

48. Pron, A.; Grenoud, F.; Menardo, C.; Nechschein, M. *Synth. Met.* **1988**, *24*, 193.

49. Armes, S. P.; Miller, J. F. *Synth. Met.* **1988**, *24*, 385.

50. Rapi, S.; Bocchi, V.; Gardini, G. P. *Synth. Met.* **1988**, *24*, 217.

51. Inoue, M. B.; Velazouez, E. F.; Inoue, M. *Synth. Met.* **1988**, *24*, 223.

52. Inoue, M.; Navarro, R. E.; Inoue, M. B. *Synth. Met.* **1989**, *30*, 199.

53. Groenendaal, L.; Peerlings, H.W.I.; van Dongen, J. L. J.; Havinga, E. E.; Vekemans, J.A. J. M.; Meijer, E. W. *Macromolecules*, **1995**, *28*, 116.

54. Pomerantz, M.; Yang, H.; Cheng, Y. *Macromolecules*, **1995**, *28*, 5706.

55. Bao, Z.; Chen, Y.; Cai, R.; Yu,. L. *Macromolecules*, **1993**, *26*, 5281.

56. Greiner, A.; Heitz, W. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 581.

57. Martelock, H.; Greiner, A.; Heitz, W. *Makromol. Chem.* **1991**, *192*, 967.

58. Suzuki, M.; Saegusa, T. *Macromolecules*, **1990**, *23*, 1574.

59. Weitzel, H. P.; Mullen, K. *Makromol. Chem.* **1990**, *191*, 2837.

60. Bao, Z.; Chan, W.; Yu, L. *Chem. Mater.* **1993**, *5*, 2.

61. Bao, Z.; Chan, W. K.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426.

62. Rehahn, M.; Schluter, A. D.; Wegner, G.; Feast, W. *Polymer* **1989**, *30*, 1060.

63. Rehahn, M.; Schlutor, A. D.; Wegner, G. *Makromol. Chem., Rapid. Commun.* **1990**, *11*, 535.

64. Rehahn, M.; Schluter, A. D.; Wegner, G. *Makromol. Chem.* **1990**, *191*, 1991.

65. Martina, S.; Schluter, A. D. *Macromolecules*, **1992**, *25*, 3607.

66. Martina, S.; Enkelmann, V.; Schluter, A. D.; Wegner, G. *Synth. Met.* **1991**, *41*, 403.

67. Martina, S.; Enkelmann, V.; Schluter, A. D.; Wegner, G. *Synthesis*, **1991**, 613.

68. Martina, S.; Enkelmann, V.; Schluter, A. D.; Wegner, G. *Synth. Met.* **1992**, *51*, 299.

69. Martina, S.; Enkelmann, V.; Schluter, A. D.; Wegner, G.; Zotti, G.; Zerbi, G. *Synth. Met.* **1993**, *55*, 1096.

70. Zotti, G.; Martina, S.; Schluter, A. D.; Wegner, G. *Adv. Mat.* **1993**, *4*, 798.

71. Zerbi, G.; Veronelli, M.; Martina, S.; Schluter, A. D.; Wegner, G. *Adv. Mat.* **1994**, *6*, 385.

72. Gin, D. L.; Conticello, V. P.; Guffs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3167.

73. Mc Cullough, R. D.; Lower, R. D. *J. Chem. Soc. Chem. Commun.* **1992**, 70.

74. Mc Cullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904.

75. Mc Cullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608.

76. Mc Cullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910.

77. Mc Cullough, R. D.; Jayaraman, M. J. *Chem. Soc., Chem. Commun.* **1995**, 135.
78. Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087.
79. Chen, T.-A.; Rieke, R. D. *Synth. Met.* **1993**, *60*, 175.
80. Chen, T.-A.; O'Brien, R. A ; Rieke, R. D. *Macromolecules*, **1993**, *265*, 3462.
81. Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.
82. Wessling, R. A. *J. Polym. Sci. Polym. Symp.* **1985**, *72*,55.
83. Gagnon, D. R.; Capistran, J. D.; Karasz, F. E.; Lenz, R. W. *Polymer*, **1987**, *28*, 567.
84. Murase, I.; Ohnishi, T.; Noguchi, T.; Hirroka, M. *Synth. Met.* **1987**, *17*, 639.
85. Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D.D.C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47.
86. Jin, J.-I.; Park, C.-K.; Shim, H.-K. *Macromolecules*, **1993**, *26*, 1799.
87. Jin, J.-I.; Lee, Y.-H.; Shim, H.-K. *Macromolecules*, **1993**, *26*, 1805.
88. Scherf, U.; Mullen, K. *Synthesis*, **1992**, 23
89. Yang, C.-J.; Jenekhe, S. A. *Macromolecules*, **1995**, *28*, 1180.
90. Hall, Jr. H. K.; Padias, A. B.; Williams, P. A.; Gosau, J.-M.; Boone, H. W.; Park, D.-K. *Macromolecules*, **1995**, *28*, 1.
91. Diaz, A. F.; Kánazawa, K.. K.; Gardini, G. P.; *J. Chem. Soc. Chem. Commun.* **1979**, 635.
92. Kanazawa, K. K.; Diaz, A. F.; Geiss, R. H.; Gill, W. D.; Kwak, J. F.; Robott, J. F.; Street, G. B. *J. Chem. Soc., Chem. Commun.* **1979**, 854.
93. Tourillon, G. T.; Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173.
94. Waltman, R. S.; Bargon, J.; Diaz, A. F. *J. Phys. Chem.* **1983**, *87*, 1459.

95. Yamamoto, T.; Sanechiraand, K.; Yamamoto, A. *J. Polym. Sci. Polym. Lett. Ed.* **1980**, *18*, 9.

96. Tourillon, G.; Garnier, F. *J. Electrochem. Soc.* **1983**, *130*, 2042.

97. Bargon, J.; Mohmand, M.; Waltman, R. J. *IBM J. Res. Develop.* **1987**, *27*, 330.

98. Bargon, J.; Mohmand, M.; Waltman, R. *J. Mol. Cryst. Liq. Cryst.* **1983**, *93*, 279.

99. McDiarmid, A. G.; Chiang, M. C.; Harpen, M.; Huang, W. S.; Krawczyk, J. R.; Mammone, R. J. Mu, S. L.; Somasiri, N. L. D.; Wu, W. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **1984**, *25*, 248.

100. Kobayashi, T.; Yoneyama, H.; Tamura, H. *J. Electroanal. Chem.* **1984**, *177*, 281.

101. Sasaki, K.; Kaya, M.; Yawo, J.; Kitani, A.; Kunai, K. *J. Electroanal. Chem.* **1981**, *215*. 401.

102. Rubenstein, I.; Sabatani, E.; Rashpon, J. R. *J. Electrochem. Soc.* **1987**, *134*, 3078.

103. Mengoli, G.; Musiani, M.M. *J. Electrochem. Soc.* **1987**, *134*, 6436.

104. Suchira, E.T.; Nishide, H.; Yamamoto, K.; Oshida, S. *Macromolecules*, **1987**, *20*, 2315.

105. Garnier, F.; Tourillon, G.; Gazard, M.; Dubois, J.C. *J. Electroanal. Chem.* **1983**, *148*, 299.

106. Said, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc. Chem. Commun.* **1985**, 713.

107. Roncali, J.; Garnier, F. *Nouv. J. Chim.* **1986**, *10*, 237.

108. Waltman, R. J.; Diaz, A. F.; Bargon, J. *J. Electrochem. Soc.* **1984**. *131*. 1452.

109. Waltman, R. J.; Diaz, A. F.; Bargon, J. *J. Electrochem. Soc.* **1985**. *132*. 831.

110. Segawa, H.; Shimidzu, T.; Honda, K. *J. Chem. Soc. Chem. Commun.* **1989**, 132.

111. Kern, J.- Marc.; Sauvage, J.- P. *J. Chem. Soc. Chem. Commun.* **1989**, 657.

112. Iyoda, T.; Kitano, M.; Shimidzu, T. *J. Chem. Soc. Chem. Commun.* **1991**, 1618.

113. Catellani, M.; Caronna, T.; Meille, S.V. *J. Chem. Soc. Chem. Commun.* **1985**, 713.

114. Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

115. Bredas, J. L. *J. Chem. Phys.* **1985**, *82*, 3808.

116. Bredas, J. L. *Springer Solid State Sci.* **1985**, *63*, 166.

117. Lee, Y.-K.; Kertesz, M.; Elsenbaumer, R. L. *Chem. Mter.* **1990**, *2*, 526.

118. Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 3382.

119. Wudl, F.; Kobayashi, M.; Heeger, A. J.; Colaneri, N. *J. Chem. Phys.* **1985**, *82*, 5717.

120. Pomerantz, M.; Chaloner-Gill, B.; Harding, L. O. Tseng, J. J.; Pomerantz, W. O. *J. Chem. Soc. Chem. Commun.* **1992**, 1672.

121. Pomerantz, M.; Chaloner-Gill, B.; Harding, L. O. Tseng, J. J.; Pomerantz, W. O. *Synth. Met.* **1993**, *55-57*, 960.

122. Jenekhe, S. A. *Nature*, **1986**, *322*, 345.

123. Wudl, F.; Patil, A. O. *Macromolecules*, **1988**, *21*, 540.

124. Becker, R.; Blochl, G.; Braunling, H. *Springer Ser. Solid State, Sci.* **1989**, *91*, 465.

125. Jira, H. R.; Braunling, H. *Synth. Met.* **1987**, *17*, 691.

126. Hanack, M.; Schmid, U.; Echinger, S.; Teichert, F.; Hieber, J. *Synthesis*, **1993**, 634.

127. Lorcy, D,; Cava, M. P. *Adv. Mater.* **1992**, *4*, 562.

128. Bauerle, P.; Gotz, G.; Emerle, P.; Port, H. *Adv. Mater.* **1992**, *4*, 564.

129. Musmanni, S.; Ferraris, J. P. *J. Chem. Soc. Chem. Commun.* **1993**, 172.

130. Tanaka, S.; Yamashita, M. *Synth. Met.* **1993**, *55-57*, 1251.

131. Zhou, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7371.

132. Lambert, T. L.; Ferraris, J. P. *J. Chem. Soc. Chem. Commun.* **1991**, 752.

133. Ferraris, J. P.; Lambert, T. L. *J. Chem. Soc. Chem. Commun.* **1991**, 1268.

134. Ferraris, J. P.; Bravo, A.; Kim, W.; Hrncir, D. C. *J. Chem. Soc. Chem. Commun.* **1994**, 991.

135. Kundu, S.; Rahman, M. S.; Maiti, S. *J. Polym. Mater.* **1993**, 10.

136. Kitamura, C.; Tanaka, S.; *J. Chem. Soc. Chem. Commun.* **1994**, 1585.

137. Karikomi, M.; Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6791.

138. Ono, K.; Tanaka, S.; Yamashita, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1977.

139. Susiki, T.; Fujii, H.; Yamashita, Y.; Kabuto, C.; Tanaka, S.;Harasawa, M.; Mukai, T.; Miyashi, T. *J. Am. Chem. Soc.* **1992**, *114*, 3034.

140. Yamashita, Y.; Ono, K.; Tanaka, S.; Imaeda, K. *J. Chem. Soc. Chem. Commun.* **1993**. 1803.

141. Tanaka, S.; Yamashita, Y. *Synth. Met.* **1995**, *69*, 599.

142. Alberti, A.; Favaretto, L.; Seconi, G. *J. Chem. Soc. Perkin. Trans. 2*, **1990**, 931.

143. Barbarella, G.; Zambianchi, M.; Bogini, A.; Antolini, L. *Adv. Mater.* **1993**, *5*, 834.

144. Distefano, G.; Colle, M. D.; Jones, D.; Zambianchi, M.; Favaretto, L.; Modelli, A. *J.Phys. Chem.* **1993**, *97*, 3504.

145. Brisset, H.; Thobie-Gautier, C.; Jubault, M.;Gorgues, A.; Roncali, J. *J. Chem. Soc. Chem. Commun.* **1994**, 1305.

146. Brisset, H.; Thobie-Gautier, C.; Jubault, M.;Gorgues, A.; Roncali, J. *J. Chem. Soc. Chem. Commun.* **1994**, 1765.

147. Roncali, J.; Thobie-Gautier, C. *Adv. Mater.* **1994**, *6*, 846.

148. Yamada, S.; Tokito, S.; Tsutsui, T.; Saito, S. *J. Chem. Soc. Chem. Commun.* **1987**, 1448.

149. Roncali, J.; Thobie-Gautier, C.; Elandaloussi, E. H.; Frere, P. *J. Chem. Soc. Chem. Commun.* **1994**, 2249.

150. Peierls, R. E. *Quantum Theory of Solids*, Oxford University Press, London, **1955**, 108..

151. Bohnen, A.; Koch, K. H.; Luttke, W.; Mullen, K. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 525.

152. Cheng, H.; Elsenbaumer, R. L. *J. Chem. Soc. Chem. Commun.* **1995**, 1451.

153. Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858.

154. Patil, A. O.; Ikenoue, Y.; Basescu, N.; Colaneri, N.; Chen, J.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1987**, *20*, 151.

155. Sundaresan, N. S.; Basak, S.; Pomerantz, M.; Reynolds, J. R. *J. Chem. Soc. Chem. Commun.* **1987**, 621.

156. Havinga, E. E.; van Horssen, L. W.; ten Hoeve, W.; Wynberg, H.; Meijer, E. W. *Polym. Bull.* **1987**, *18*, 277.

157. Havinga, E. E.; ten Hoeve, W.; Meijer, E. W.; Wynberg, H. *Chem. Mater.* **1989**, *1*, 650.

158. Ge, H.; Gilmore, K. J.; Ashraf, S. A.; Too, C. O.; Wallace, G. G. *Polymer*, **1993**, *34*, 2007.

159. Ikenoue, Y.; Chiang, J.; Patil, A. O.; Wudl, F.; Heeger, A. J. *Synh. Met.* **1988**, *110*, 2983.

160. Ikenoue, Y.; Uotani, N.; Patil, A. O.; Wudl, F.; Heeger, A. J. *Synh. Met.* **1989**, *30*, 305.

161. Ikenoue, Y.; Saida, Y.; Kira, M.; Tomozawa, H.; Yashima, H.; Kobayashi, M. *J. Chem. Soc. Chem. Commun.* **1990**, 1694.

162. Chen, S. -A.; Hua, M. -Y. *Macromolecules*, **1993**, *26*, 7108.

163. Arroyo, M. I.; Diaz-Quijada, G. A.; Abdou, M. S. A.; Holdcroft, S. *Macromolecules*, **1995**, *28*, 975.

164. Gerardo, A.; Diaz-Quijada, B.; Pinto, M.; Holdcroft, S. *Macromolecules*, **1996**, *29*,5416.

165. Chen, S. -A.; Hua, M. -Y. *Macromolecules*, **1996**, *29*, 4919.

166. Yue, J.; Epstein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 2800.

167. Yue, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. J.; Macdiarmid, A. G. *J. Am. Chem. Soc.* **1991**, *113*, 2665.

168. Hany, P.; Genies, E. M.; Santier, C. *Synth. Met.* **1989**, *31*, 369.

169. Bergeron, J. Y.; Chevalier, J. W.; Dao, L. H. *J. Chem. Soc. Chem. Commun.* **1990**, 180.

170. Chen, S. -A.; Hwang, G.-W. *J. Am. Chem. Soc.* **1994**, *116*, 7939.

171. De Armitt, C.; Armes, S. P.; Winter, J.; Uribe, F. A.; Gottesfeld, S.; MombourQuette, C. *Polymer*, **1993**, *34*, 158..

172. Ng, S. C.; Chan, H. S. O.; Huang, H. H.; Ho, P. K. H. *J. Chem. Soc. Chem. Commun.* **1995**, 1327.

173. Chan, H. S. O.; Ho, P. K. H.; Ng, S. C.; Tan, B. T. G.; Tan, K. L. *J. Am. Chem. Soc.* **1995,** *117*, 8517.

174. Wrighton, M. S.; *Comments Inorg. Chem.* **1985**, *4*, 269.

175. *Molecular Electronic Devices*; Carter, F. L.; Ed,; Marcel Dekker: New York, **1987**.

176. *Molecular Electronic Devices II*; Carter, F. L.; Ed,; Marcel Dekker: New York, **1987**.

177. Hopfied, J. J.; Onuchic, J. N.; Beratan, D. N. *Science* **1988**, *241*, 817.

178. *Supramolecular Chemistry I- Directed Synthesis and Molecular Recognition*; Weber, E., Ed.; Springer-Verlag, New York, **1993**.

179. Marsella, M. J.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 12214.

180. Marsella, M. J.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1994**, *116*, 9347.

181. Swager, T. M.; Marsella, M. J.; *Adv. Mater.* **1994**, *6*, 595.

182. Youssoufi, H. K.; Hmyene, M.; Garnier, F.; Delabouglise, D. *J. Chem. Soc. Chem. Commun.* **1993**, 1550.

183. Bauerle, P.; Scheib, S. *Adv. Mater.* **1993**, *5*, 848.

184. Thackeray, J. W.; Wrighton, M. S. *J. Phys. Chem.* **1986**, *90*, 6674.

185. Zotti, G. *Synth. Met.* **1992**, *51*, 373.

186. Marsella, M. J.; Newland, R. J.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 9842.

187. Marsella, M. J.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 9833.

188. Levesque, I.; Leclerc, M. *J. Chem. Soc. Chem. Commun.* **1995**, 2293.

189. Brockmann, T. W.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 7435.

190. Brockmann, T. W.; Tour, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 4437.

191. Treibs, A.; Fritz, G. *Liebigs Ann. Chem.* **1957**, *611*, 162.

192. Sprenger, H. E.; Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 894.

193. Sprenger, H. E.; Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 553.

194. Sprenger, H. E.; Ziegenbein, W. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 530.

195. Schmidt, A. H. *Synthesis* **1980**, 961.

196. Schmidt, A. H. In *Oxocarbons*; West, R., Ed.; Academic Press: New York, **1980**; Chapter 10.

197. Law, K.- Y.; Bailey, F. C. *J. Imaging Sci.* **1987**, *31*, 172.

198. Tam, A. C. *Appl. Phys. Lett.* **1980**, *37*, 978.

199. Morel, D. L.; Stogryn, E. L.; Piechowski, A. P. *J. Phys. Chem.* **1984**, *88*, 923.

200. Piechowski, A. P.; Bird, G. R.; Morel, D. L.; Stogryn, E. L. *J. Phys. Chem.* **1984**, *88*, 934.

201. Emmelius, M.; Pawlowski, G.; Vollmann, H. W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1445.

202. Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449 and references cited therein.

203. Kamat, P. V.; Das, S.; Thomas, K. G.; George, M. V. *Chem. Phys. Lett.* **1991**, *178*,75.

204. Patrick, B.; George, M. V.; Kamat, P. V.; Das, S.; Thomas, K. G. *J. Chem. Soc. Faraday Trans.*, **1992**, *88*, 671.

205. Das, S.; Kamat, P. V.; Dela Barre, B.; Thomas, K. G.; Ajayaghosh, A.; George, M. V. *J. Phys. Chem.* **1992**, *96*, 10327.

206. Das, S.; Thomas, K. G.; Kamat, P. V.; George, M. V. *Proc. Indian Acad. Sci. (Chem. Sci.)*, **1993**, *105*, 513 and references cited therein.

207. Das, S.; Thomas, K. G.; Thomas, K. J.; George, M. V.; Bedja, I.; Kamat, P. V. *Anal. Proc.* **1995**, *32*, 213.

208. Sauve, G.; Kamat, P. V.; Thomas, K. G.; Thomas, K. J.; Das, S.; George, M. V. *J. Phys. Chem.* **1996**, *100*, 2117.

209. Treibs, A.; Jacob, K. *Justus Leibigs Ann. Chem.* **1966**, *699*, 153.

210. Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Polym. Bull.* **1992**, *29*, 119.

211. Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Synth. Met.* **1993**, *55-57*, 299.

212. Yu, L.; Chen, M.; Dalton, L. R. *Polymer*, **1991**, *32*, 1369.

213. Manecke, G.; Gauger, *J. Makromol. Chem.* **1969**, *125*, 231.

214. Gauger, J.; Manecke, G. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 898.

215. Manecke, G.; Gauger, J. *Tet. Lett.* **1967**, 3509.

216. Manecke, G.; Gauger, J. *Tet. Lett.* **1968**, 1139.

217. Gauger, J.; Manecke, G. *Chem. Ber.* **1970**, *103*, 2696.

218. Gauger, J.; Manecke, G. *Chem. Ber.* **1970**, *103*, 3553..

219. Neuse, E. W.; Green, B. R. *Leibigs Ann. Chem.* **1973**, 619.

220. Neuse, E. W.; Green, B. R. *Leibigs Ann. Chem.* **1973**, 633.

221. Neuse, E. W.; Green, B. R. *Polymer* **1974**, *15*, 339.

222. Brocks, G. *J. Chem. Phys.* **1995**, *102*, 2522.

223. Brocks, G.; Tol, A. *J Phys. Chem.* **1996**, *100*, 1838.

CHAPTER 2

SYNTHESIS AND PROPERTIES OF SOLUBLE, LOW BANDGAP π-CONJUGATED COPOLYMERS DERIVED FROM SQUARIC ACID AND ALKYLPYRROLES

2.1. Introduction

Designing of novel organic π-conjugated polymers and investigation of their electronic, optical and related properties constitute important areas of research in contemporary polymer chemistry and material related science. π-Conjugated oligomers and polymers play vital role as advanced technological materials such as electrical semiconductors, non-linear optical (NLO) materials and as photo- and electroluminescent materials. Therefore, considerable attention has been paid on the synthesis of soluble and processable π-conjugated polymers with low bandgap energy (Eg), due to their intrinsic semiconductivity, NLO activity and electroluminescent properties.[1-4] Synthesis of such polymers and their precursors are usually achieved by multistep synthetic procedures and the resultant polymers, in most of the cases, are insoluble and intractable, thereby limiting their practical applications. Therefore, designing of viable routes for the synthesis of soluble and processable polymers with low Eg and methods to control their optical and electronic properties have great significance.

Based on theoretical calculations and modelling, several strategies have been developed for the design of low bandgap polymers.[5-7] Novel approaches such as tailoring of the monomer structure in order to increase the quinoid character of the resulting π-conjugated polymers, use of donor-acceptor monomers and rigidification of the π-conjugated polymer backbone are found to be effective in lowering the bandgap energies.[8-16] Another practical approach in the designing of low Eg polymers would be the use of molecules having low HOMO-LUMO separation as the building blocks. In this way low bandgap energy can be achieved even at the oligomeric stage. Organic dye molecules would be the ideal candidates for such a purpose because of their low HOMO-LUMO separation and interesting optical and electronic properties.

3,4-Dihydroxy-3-cyclobutene-1,2-dione (squaric acid) is known to undergo facile condensation with electron rich aromatic molecules such as N,N-dialkylanilines, phenols, pyrroles and benzothiazoles to form highly coloured zwitterionic (betaine) dyes, commonly referred to as squaraine dyes.[17-21] This class of organic dyes exhibits sharp and intense absorption in the visible region in solution. In the solid state, due to the crystal packing and strong intermolecular charge-transfer (donor-acceptor) interactions, the absorption becomes very broad with bathochromic shift to the NIR region (panchromatic shift). These optical absorption characteristics have made squaraines very attractive for a variety of applications such as in xerography,[22,23] organic solar cells [24,25] and for optical data storage.[26]

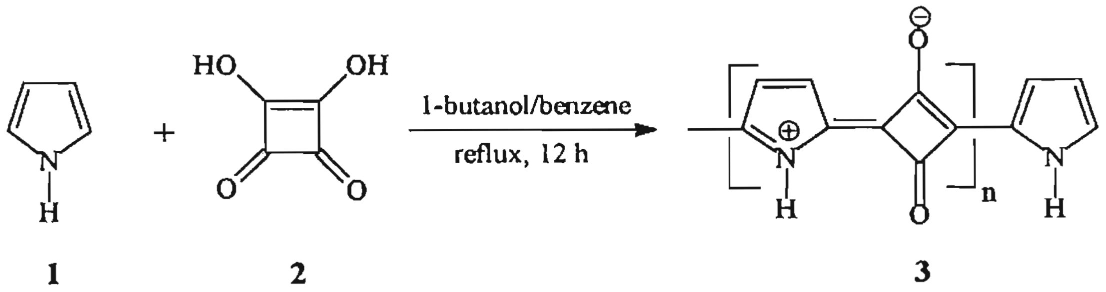
Due to the strong donor-acceptor interaction and low HOMO-LUMO energy gap, squaraine dyes would be ideal candidates as building blocks for the synthesis of low bandgap conjugated polymers. This can be achieved by the polycondensation of squaric acid with electron rich aromatic compounds having more than one reaction centers. The earliest attempt towards the synthesis of a macromolecular squaraine was made way back in 1965 by Treibs and Jacob.[27,28] Later, Havinga *et al.* have synthesized low bandgap polysquaraines and polycroconaines by the condensation of squaric acid and croconic acid, respectively with benzobisthiazole.[29,30] The low Eg and the intrinsic semiconductivity of these polymers are reported to arise from the regular alternation of strong electron donor and acceptor moieties in the conjugated polymer backbone.

The significance of squaraines in designing low Eg conducting polymers is gaining the attention of both experimental and theoretical chemists. Ab initio calculations by Brocks *et al.* have predicted the factors that control the size of the bandgap energy in this class of polymers.[31,32] Car-Parrinello techniques have been used to optimize both the electronic and the geometrical structures of several possible polysquaraines and have observed that bandgaps ranging from 2.3 to as low as 0.2 eV can be achieved by choosing appropriate polymer repeat units. Encouraged by this information, we felt that it would be worthwhile to synthesize a few soluble macromolecular analogues of pyrrole-derived squaraines[33] which have not received much attention in recent years, for the evaluation of their optical and conducting properties.

2.2. Results and Discussion

Squaric acid is known to condense with pyrrole resulting in highly insoluble and intractable powdery materials as shown in Scheme 1.[27,28] The structural identity and the physical properties of these materials are not known in the literature. In order to gather information on the structure and properties of such materials, it would be necessary to improve their solubility in different solvents. A common approach to enhance the solubility of π-conjugated polymers is to incorporate long alkyl chains on to the polymer backbone. This could be achieved by using monomers substituted with appropriate alkyl groups. Therefore, in the present study, several pyrrole derivatives with long alkyl chains at 1- or 3-

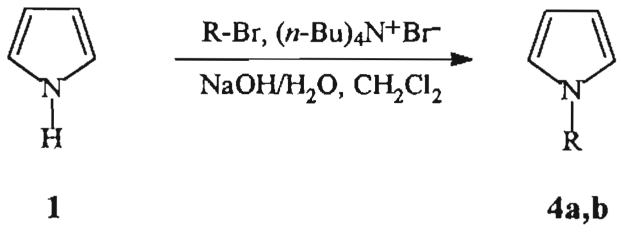
positions of the pyrrole ring were chosen as the starting materials which were prepared as per known or modified literature procedures.



Scheme 1

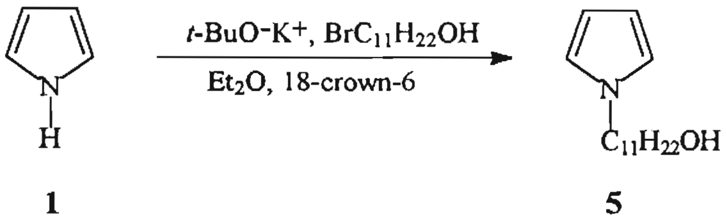
2.2.1. Synthesis of pyrrole derivatives

N-Octyl- and N-dodecylpyrroles were prepared under standard phase transfer conditions according to Scheme 2.[34] 11-(1-Pyrrolyl)undecanol was prepared by the reaction of pyrrole with 11-bromo-1-undecanol in the presence of potassium *t*-butoxide and 18-crown-6 (Scheme 3).[35] 3-Octyl- and 3-dodecyl–pyrroles were prepared from 1-(phenylsulfonyl)pyrrole by the Friedel-Crafts reaction with the corresponding acid chlorides, followed by Clemmenson reduction of the ketones **7a,b** and the subsequent alkaline hydrolysis as depicted in Scheme 4.[36,37] 1-Dodecyl-2,4-dimethylpyrrole (**10**) was obtained by the reaction of 2,4-dimethylpyrrole with 1-bromododecane under phase transfer conditions (Scheme 5). All pyrrole derivatives were purified by column chromatography and characterized on the basis of spectral data and analytical results.



4a, R = $(CH_2)_7CH_3$
4b, R = $(CH_2)_{11}CH_3$

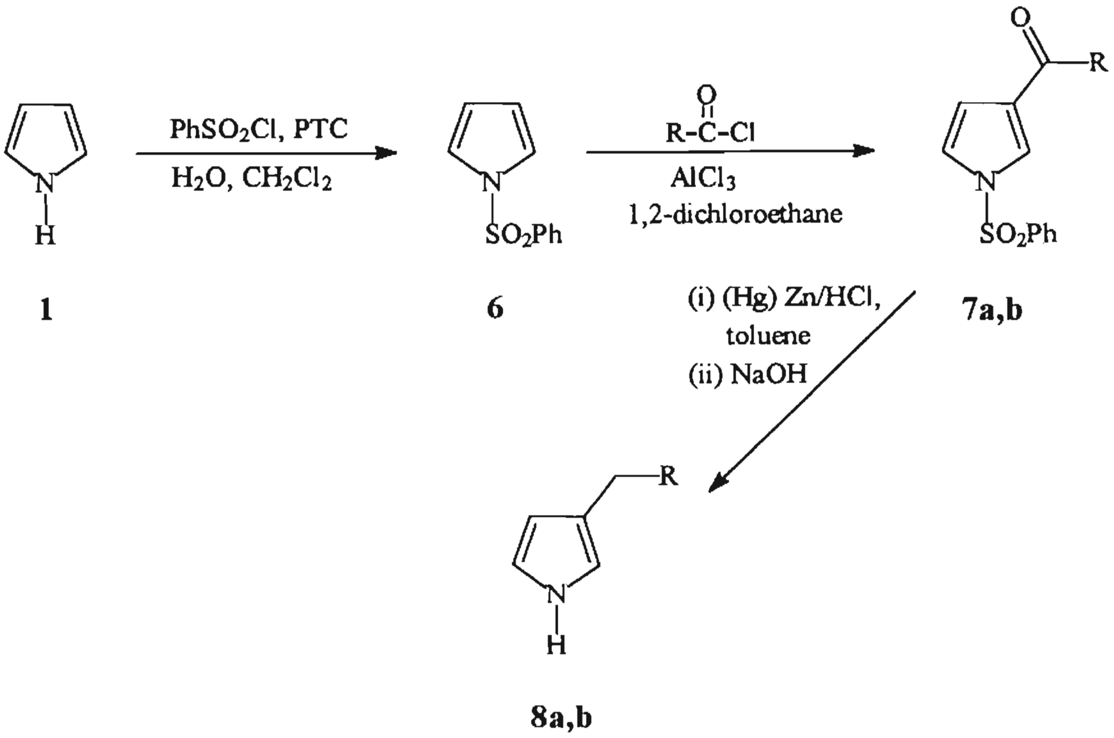
Scheme 2



Scheme 3

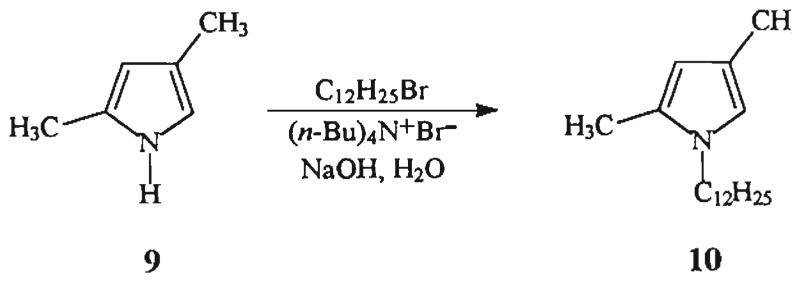
2.2.2. Preparation of polysquaraines

The polysquaraines under investigation were obtained by the polycondensation of various pyrrole derivatives with squaric acid. These reactions are examples of condensation copolymerization between two different monomers leading to the formation of A-B type copolymers. These copolymerizations were carried out under various experimental conditions such as different solvent combinations and temperatures. In a typical procedure, condensation of the pyrrole moiety and squaric acid (1:1 mol ratio) in a mixture of 1-butanol and benzene



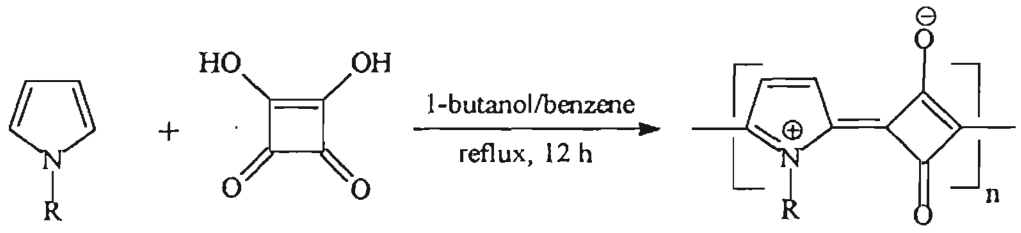
a, R = $(CH_2)_6CH_3$
b, R = $(CH_2)_{10}CH_3$

Scheme 4



Scheme 5

under azeotropic removal of water, afforded a deep blue solution, along with small amounts of a ribbon-like insoluble product (Scheme 6). The deep blue solution, was concentrated under reduced pressure and treated with diethyl ether to give a product (60-65% yield), which was further purified by dissolving it in chloroform and reprecipitating with diethyl ether. The precipitate, thus obtained was soluble in solvents such as DMF, DMSO, THF and chloroform. GPC analysis showed that the number average molecular weight (M_n) of such polymeric products ranged between 4000-6000, indicating a low degree of polymerization.

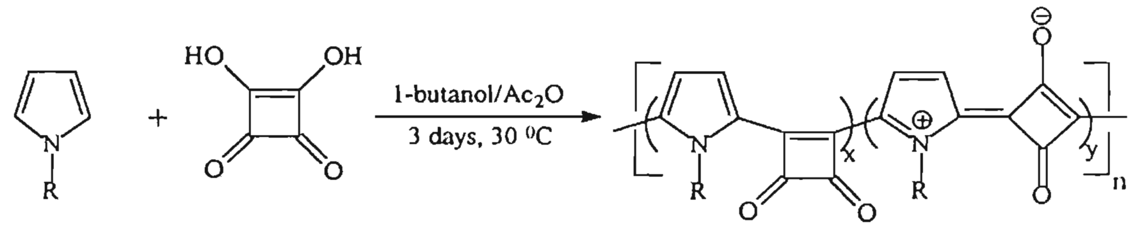


4a,b or **5** **2** **11a-c**

a, R = C_8H_{17}
b, R = $C_{12}H_{25}$
c, R = $C_{11}H_{22}OH$

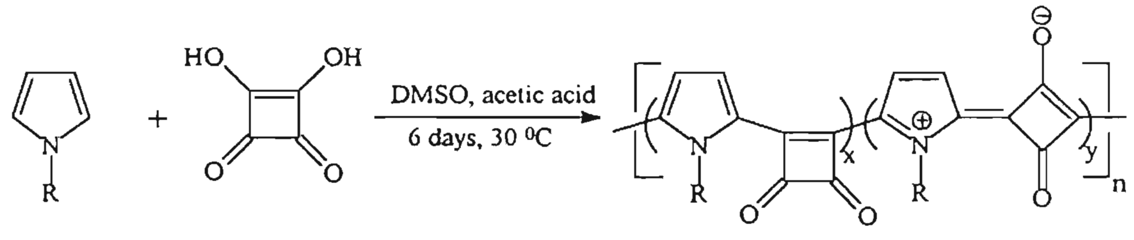
Scheme 6

Since, the condensation of squaric acid with N-alkylpyrroles under the normal reaction conditions, employed for the preparation of squaraine could not provide polysquaraines with expected solubility and molecular weights, the reaction conditions had to be modified for obtaining higher molecular weight polysquaraines with better solubility. For this purpose several solvent mixtures and reaction conditions have been tried. Better results were obtained when the condensation was performed in 1-butanol-acetic anhydride or acetic acid-DMSO mixtures at room temperature (Schemes 7 & 8). For example, condensation of squaric acid with N-octylpyrrole (1:1 mol ratio) in a mixture of acetic acid and DMSO (1:1) for 6-7 days gave a green polymeric product, which was highly soluble in a wide variety of organic solvents such as aliphatic and aromatic hydrocarbons and halogenated solvents (Scheme 8). The 3-alkylpyrroles also



4b **2** **12**

Scheme 7

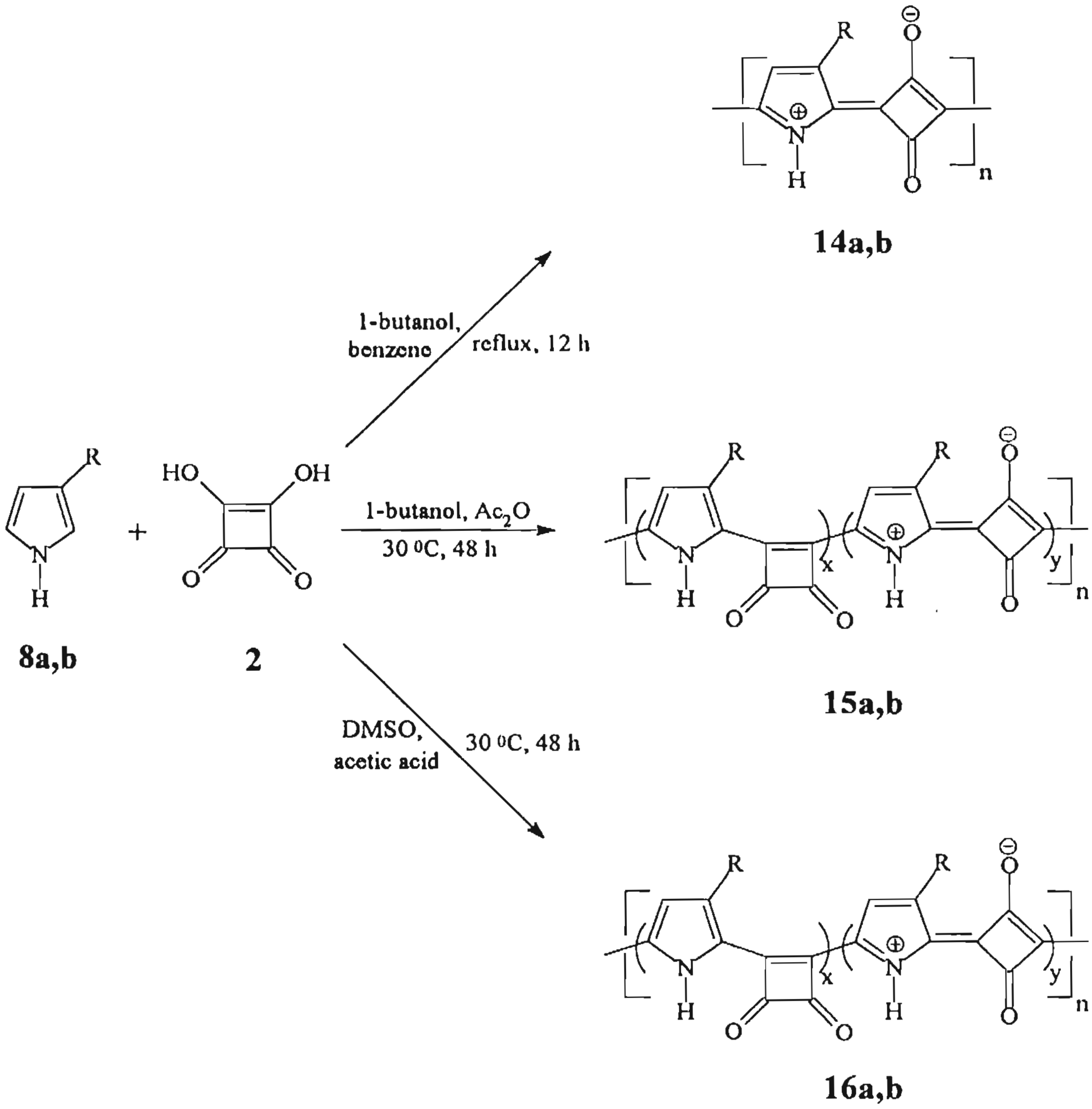


4b **2** **13**

$R = C_{12}H_{25}$

Scheme 8

reacted with squaric acid in the same way as N-alkylpyrroles, to form coloured polymeric products (Scheme 9). However, 3-alkylpyrroles are found to be more reactive than N-alkylpyrroles towards squaric acid. The polymers **16a,b** obtained

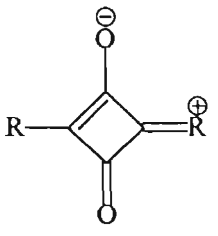


a, R = C_8H_{17}
b, R = $C_{12}H_{25}$

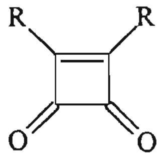
Scheme 9

in acetic acid-DMSO medium also showed better solubility in a wide range of organic solvents, as compared to those prepared from 1-butanol-benzene mixture under reflux conditions. The polymers **11a-c** and **14a,b** obtained in 1-butanol-benzene under azeotropic reflux conditions showed better solubility in polar protic solvents, whereas the polymers **13** and **16a,b** obtained in acetic acid-DMSO showed high solubility in aprotic solvents.

Even though the observed anomalies in solubility of the products obtained under various reaction conditions are not clear at this stage, it is assumed that the difference in solubility could possibly arise from the structural variations of the products. The structural variation can result from the orientational preference of squaric acid towards the pyrrole derivatives during polycondensation reactions, leading to the formation of two types of isomeric repeat units in the polymer chain. For example, an electron rich aromatic nucleophile 'R', in principle, can react with squaric acid to form two isomeric products having the structures **17** and **18**, as depicted in Chart 1. Therefore, in the case of the polycondensation reaction between squaric acid and substituted pyrroles, it is reasonable to anticipate the presence of both the isomeric structures as the integral parts of the polymeric chain. The basic difference between the polymers prepared in various solvent



17



18

Chart 1

mixtures is in the ratio between the two isomeric repeat units, which dictates their solubility and molecular weights. Increasing amounts of the 1,3-substituted zwitterionic repeat units in the polymer chain may decrease its solubility as in the case of polymers **11a-c** and **14a,b**. In order to get clear evidence for the above observations we have carried out detailed analysis of the condensation products obtained under different reaction conditions.

2.2.3. Molecular weights of polysquaraines

The molecular weights and polydispersity indices of all polymers under investigation are very much dependent on the reaction conditions, solvents and the purification procedures employed during their preparation. The molecular weights and the corresponding polydispersity indices of all polymers were determined by gel permeation chromatography (GPC), using polystyrene standards in THF and the results are indicated in Table 1. From Table 1 it is clear that the soluble polymers **11a-c** and **16a,b** have relatively low molecular weights. Considerable increase in molecular weights of the polymers was observed on changing the solvents from 1-butanol/benzene mixture to acetic acid/DMSO mixture. For example, the polymer **13** obtained from acetic acid/DMSO gave a number average molecular weight nearly double (M_n 14308) that of **11b** which is obtained from 1-butanol/benzene mixture under azeotropic reflux condition (M_n 6000). This enhancement in molecular weight can be rationalized in terms of the effect of the solvent medium in controlling the formation of the zwitterionic and the diketonic repeat units, which in turn determine the solubility of the polymers in a particular solvent. For example, **11b** due to its high content of the zwitterionic repeat units has low solubility in 1-butanol-benzene mixture and undergoes premature precipitation before attaining high molecular weight during the polycondensation.

On the other hand, the polymer **13** prepared in acetic acid-DMSO medium may contain the diketonic repeat units in considerable amounts in addition to the zwitterionic moieties. The presence of the diketonic repeat units may enhance the solubility of the condensation product **13,** thereby enhancing its molecular weight.

Table 1. Molecular weight and polydispersities of different polysquaraines

Polymer	Method of preparation	M_w	M_n	Polydispersity index (M_w/M_n)
N-DDP-co-SQA (**11b**)	1-butanol/benzene, reflux, 12 h	10800	6000	1.8
N-DDP-co-SQA (**12**)	1-butanol/Ac_2O, 30 ^{0}C, 3 days	13437	12018	1.1
N-DDP-co-SQA (**13**)	CH_3CO_2H/DMSO, 30 ^{0}C, 6 days	18118	14308	1.3
N-HDP-co-SQA (**11c**)	1-butanol/benzene, reflux, 12 h	7936	4960	1.6
3-DDP-co-SQA (**14b**)	1-butanol/benzene, reflux, 12 h	8100	4500	1.8
3-DDP-co-SQA (**15b**)	1-butanol/Ac_2O, 30 ^{0}C, 48 h	11087	10052	1.1
3-DDP-co-SQA (**16b**)	CH_3CO_2H/DMSO, 30 ^{0}C, 48 h	12283	10892	1.3

2.2.4. Spectroscopic characterization of polysquaraines under investigation

2.2.4.1. NMR spectral studies

The strong aggregation and relatively low solubility of squaraine dyes limit their detailed NMR spectral studies in many cases. The ^1H NMR spectrum of the low molecular weight polymer **11b** for example, showed the characteristic peaks due to the N-CH_2 protons of the side chain at δ 4.7. The CH_3 protons of the side chain alkyl group appeared as a broad triplet around δ 0.85. All the other protons of the alkyl chain were observed as a broad singlet around δ 1.2 (Figure 1). A

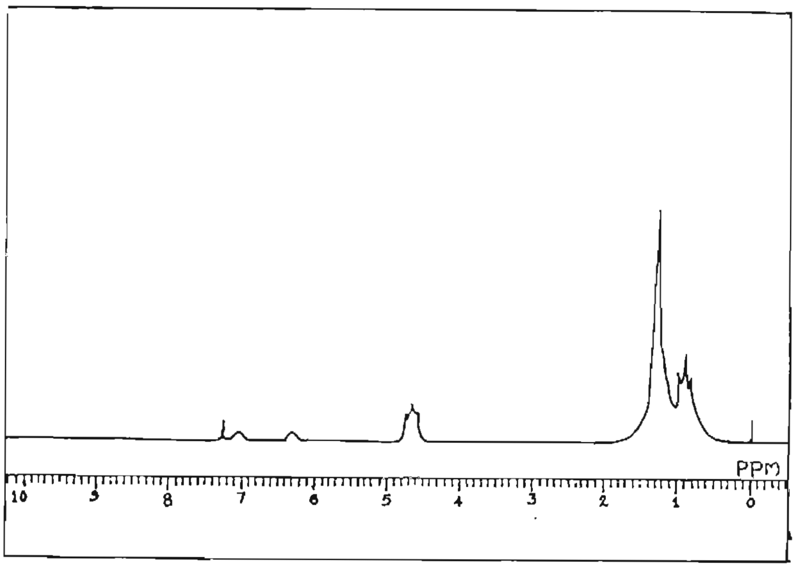


Figure 1. ^1H NMR spectrum of **11b**.

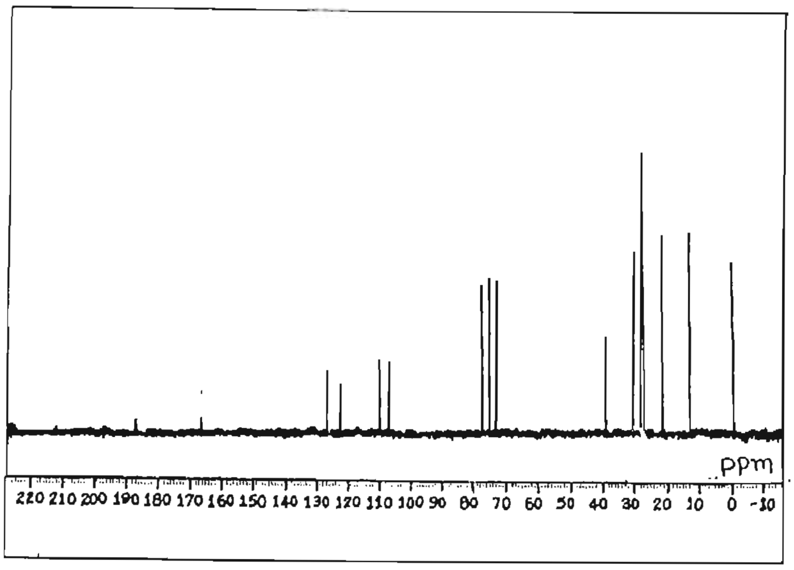
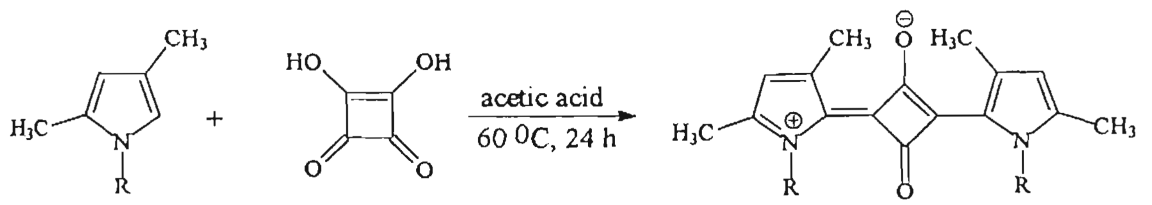


Figure 2. ^{13}C NMR spectrum of **11b**.

great difficulty encountered in the ^{1}H NMR assignment of the polymers **11a-c** is the poor resolution of the aromatic protons attached to the pyrrole ring. The reasons for this could be the strong aggregation of the highly polar polymeric dye and the high population of the side chain protons. Earlier reports on the NMR studies pertaining to the aggregation behaviour of some 3-alkyl-substituted polythiophenes have revealed that the intensity of absorption of the protons attached directly to the thiophene ring decreased drastically upon aggregation.[38] This observation supports the poor resolution of the aromatic protons in **11a-c**. The ^{13}C NMR spectrum of **11b** is in agreement with its structure except for the poor resolution of the quaternary carbon signals (Figure 2). This could probably be due to the poor solubility and strong aggregation of the polymer in $CDCl_3$. The ^{1}H NMR spectra of **13** and **16a,b** are complicated with several satellite peaks probably due to the presence of the diketonic moieties along with the zwitterionic repeat units. A clear differentiation between the polymers obtained under different experimental conditions could not be made from their ^1H NMR spectral analysis. However, the ^{13}C NMR spectra of the polymers obtained from the acetic acid/DMSO medium showed the presence of two very weak quaternary carbon signals around δ 189 and 192, which could be due to the diketonic repeat units.

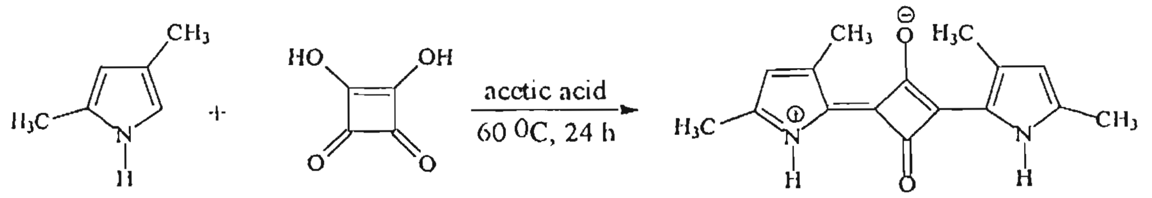
For a better insight into the structure of the polymers, two model compounds **19** and **20** were prepared as per Schemes 10 and 11 and their spectral data are compared with those of polysquaraines. The ^1H NMR of **19** in $CDCl_3$ showed two singlets at δ 2.25 and 2.65, corresponding to the protons of the four CH_3 groups attached to the two pyrrole rings (Figure 3). The N-CH_2 group



10 **2** **19**

$R = C_{12}H_{25}$

Scheme 10



9 **2** **20**

Scheme 11

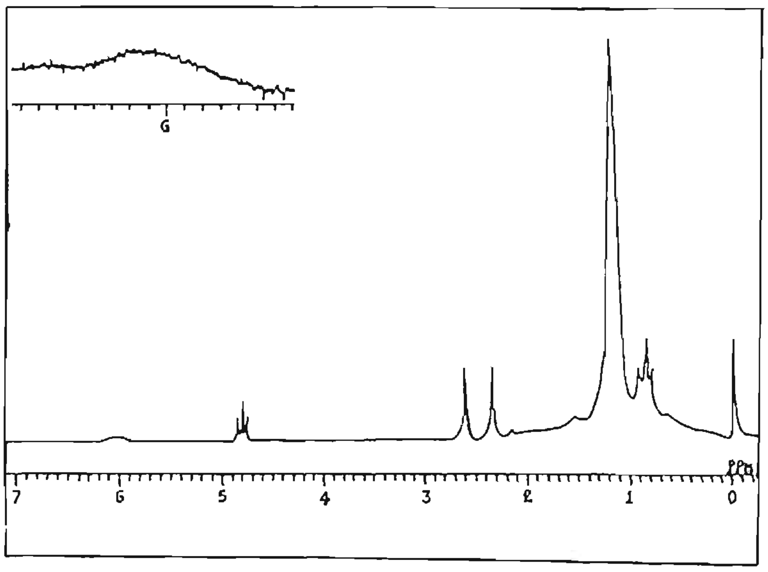


Figure 3. ^{1}H NMR spectrum of **19**.

appeared around δ 4.8 and the proton attached to the pyrrole unit appeared at δ 6.1. On the other hand, the ^{1}H NMR spectrum of the model compound **20** in which the N-alkyl chain was replaced by a hydrogen, could provide a well-resolved peak for the proton attached to the pyrrole ring (Figure 4). The poor resolution of the aromatic protons in the case of **19** could be due to the high population of the alkyl protons (δ 0.85-1.25) along with the strong tendency for aggregation as observed in the case of the analogous polysquaraine **11b**. The ^{13}C NMR spectrum of **20** (Figure 5) showed a total of eight carbon signals, which is exactly half of the total number of sixteen carbon atoms. The two carbon signals at δ 13.2 and 14.2 correspond to the four CH_3 groups, attached to the pyrrole moieties. The signals at δ 116.55, 125.30, 137.37 and 144.46 were assigned to the eight

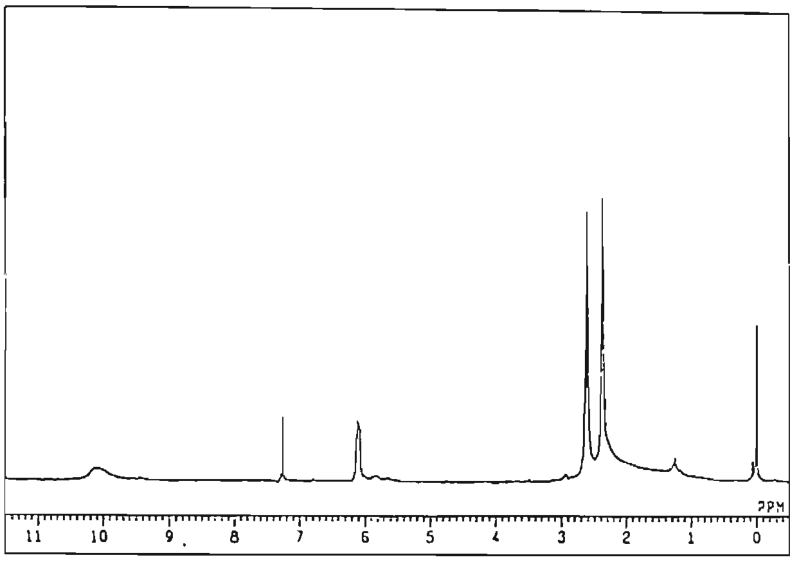


Figure 4. ^{1}H NMR spectrum of model compound **20**.

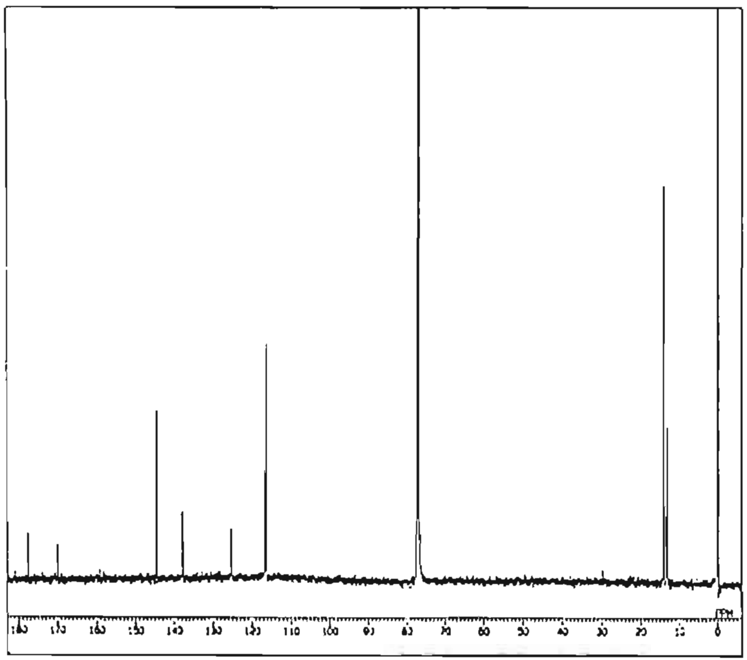


Figure 5. ^{13}C NMR spectrum of model compound **20**.

carbon atoms of the two pyrrole rings. Two signals at δ 169.90 and 177.59 were observed for the four carbon atoms of the central cyclobutene ring. The NMR spectral analyses reveal that the model compounds **19** and **20** have resonance stabilized zwitterionic structure.

2.2.4.2. Infrared spectra of polysquaraines

The principal absorption bands observed in a polymer are characteristic of its structural identity and vary with its structural composition. For example, comparison of the ratio of the intensity of absorption of distinct peaks can provide qualitative or near quantitative information on the structural composition of a copolymer. Detailed IR spectral analysis of the polysquaraines prepared under various reaction conditions were carried out for a better understanding of their structural characteristics. It is anticipated that the IR spectra of different polysquaraines will provide evidence if there is any solvent dependent orientational preference between the monomers leading to the formation of both zwitterionic and diketonic repeat units in the polymer chain. The IR spectral data of the different polysquaraines under investigation are listed in Table 2.

The IR spectra of the polymers **11a-c** and **14a,b** and their model compounds **19** and **20** which were prepared under identical experimental conditions showed a strong absorption peak between 1620-1600 cm^{-1}, corresponding to the C-O stretching frequency of a cyclobutenediylium-1,3-diolate moiety. This absorption peak is characteristic of the resonance stabilized zwitterionic structure of squaraine dyes. On the other hand, the IR spectra of the polymers **13** and **16a,b** showed two strong carbonyl absorptions around 1780 and 1720 cm^{-1}, in addition to the C-O stretching frequency at 1610 cm^{-1}. The carbonyl absorption of **13** and **16a,b** are comparable to those of a diketonic compound **21**

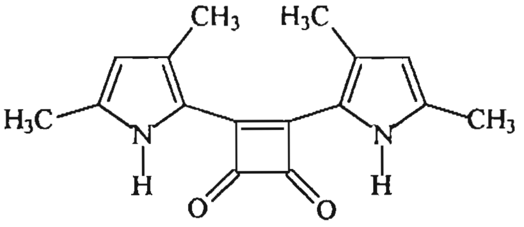
Table 2. IR spectral data (cm^{-1}) of different polysquaraines

Polymer	NH or OH stretch	Aliphatic CH stretch	C=O stretch	C-O stretch	Ring stretch
N-OCP-co-SQA (**11a**)	-	2931 2860	1787 1732 (w)	1628	1515 1464
N-DDP-co-SQA (**11b**)	-	2932 2860	1788 1739 (w)	1620	1506 1465
N-HDP-co-SQA (**11c**)	3434	2932 2859	1786 1728 (w)	1631	1511 1464
3-OCP-co-SQA (**14a**)	3360-3330	2924 2858	1760 1728 (w)	1610	1510 1460
3-DDP-co-SQA (**14b**)	3360-3330	2930 2859	1760 1725 (w)	1610	1508 1460

(Chart 2), reported earlier by Triebs and Jacob. The IR spectral values of **14b** and **16b** are compared with those of their respective zwitterionic and diketonic model compounds **20** and **21** and the data are shown in Table 3. This observation reveals that the polymer **16b,** prepared using acetic acid/DMSO solvent mixture contains diketonic repeat units in addition to the zwitterionic repeat units. This is again clear from Figure 6 in which the IR spectra of the representative polymers **11b** and **13** are compared with those of the zwitterionic squaraine dye **19** and the diketonic compound **21**.

Table 3. Comparison of IR spectral data (cm^{-1}) of **14b** and **16b** with their model compounds

Polymer/model compound	NH stretch	Aliphatic CH stretch	C=O stretch	C-O stretch	Ring stretch
3-DDP-co-SQA (**14b**)	3360-3330	2930 2859	1760 1725(w)	1610 (s)	1508 1460
3-DDP-co-SQA (**16b**)	3360-3330	2930 2859	1765 1730 (s)	1610 (m)	1508 1460
20	3230	absent	absent	1635 (s)	1535 1500
21	3290	absent	1715 1760 (s)	absent	1500



21

Chart 2

2.2.4.3. Electronic (UV-Vis-NIR) spectral studies

The electronic spectra of the different polysquaraines and their model compounds, prepared under various experimental conditions, showed significant differences. For example, N-DDP-co-SQA (**11b**), prepared in 1-butanol/benzene showed an intense blue colour with a λ_{max} around 606 nm (broad) in DMSO (Figure 7), whereas the model dye **19** showed a sharp absorption maximum at 583 nm (Figure 8). This difference in the absorption spectra of the polymer **11b** and the model dye **19** reveals that **11b** has an extended conjugation compared to **19**. On the other hand the absorption spectrum of the polymer **13**, prepared in acetic acid-DMSO medium is relatively broader compared to **11b** with an absorption maximum around 612 nm in DMSO (Figure 9). The red shift in the absorption spectrum of **13** compared to that of N-DDP-co-SQA (**11b**) can be attributed to the enhanced molecular weight and the extended conjugation in **13**.

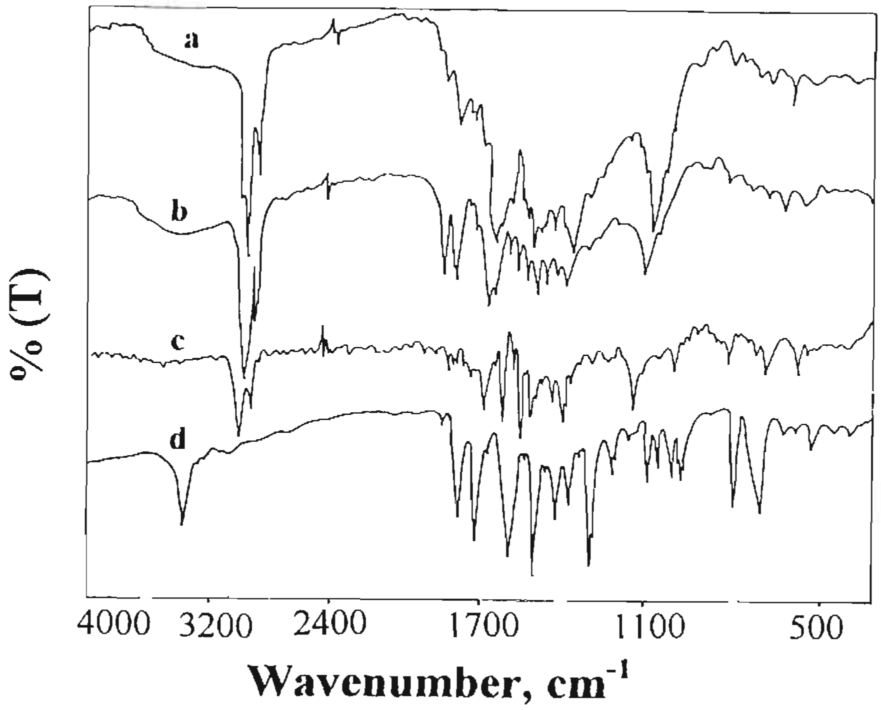


Figure 6. IR spectra of polymers (a) **11b** (b) **13** and model compounds (c) **19** and **21**.

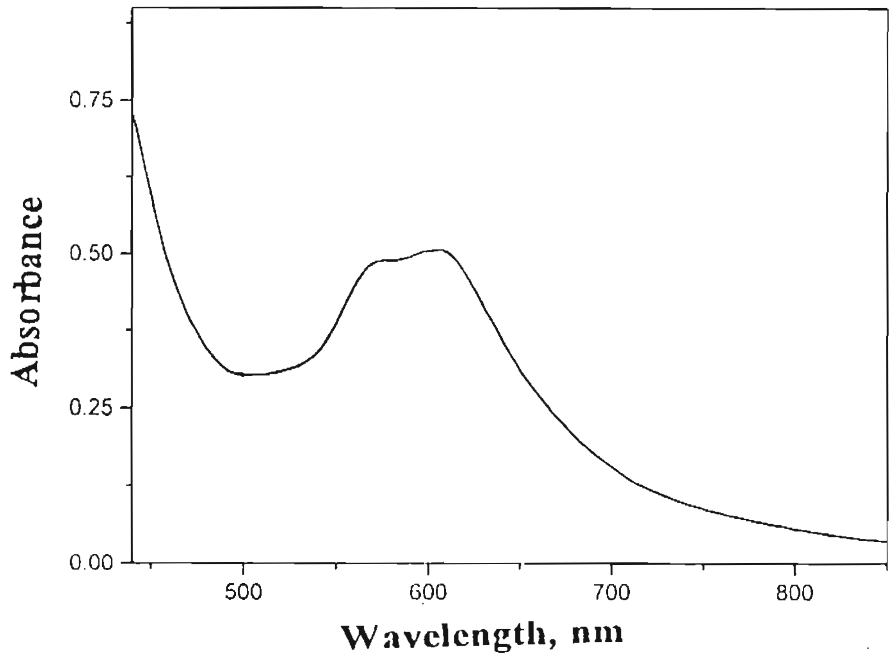


Figure 7. UV-Vis absorption spectrum of **11b** in DMSO.

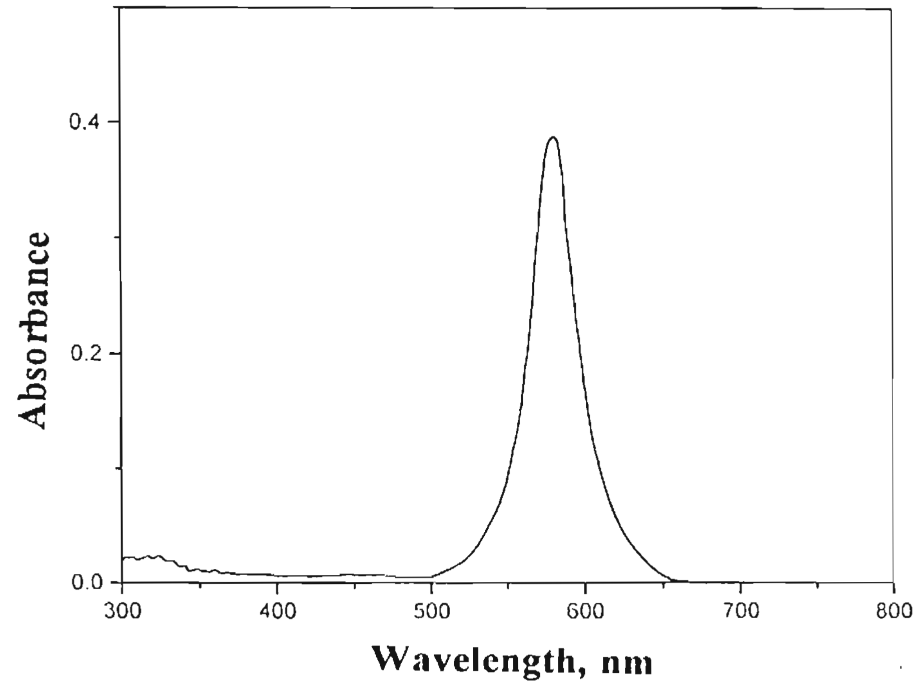


Figure 8. UV-Vis absorption spectrum of model compound **19** in DMSO.

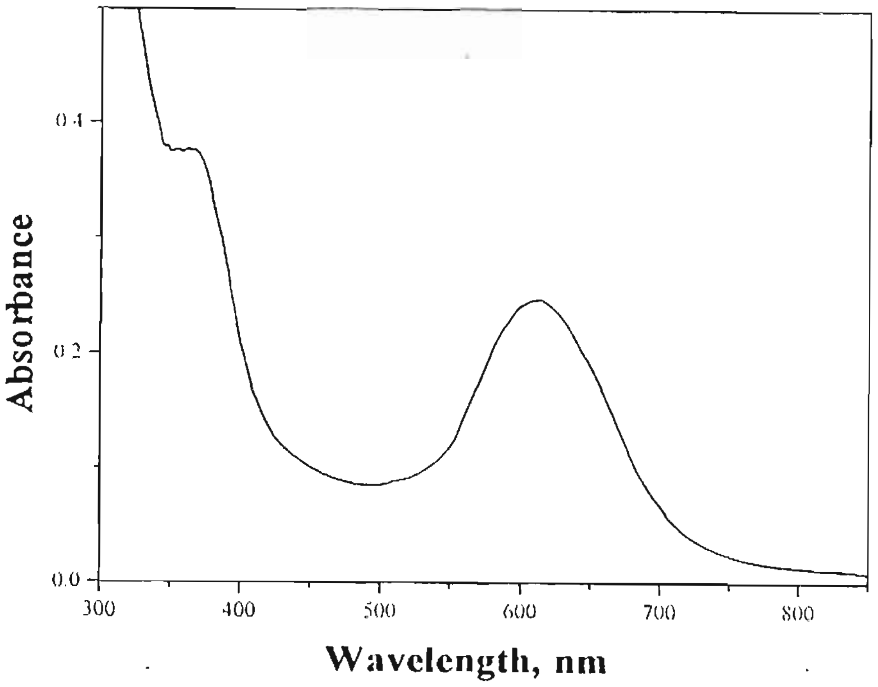


Figure 9. UV-Vis absorption spectrum of the polysquaraine **13** in DMSO.

The polymers obtained by the condensation of 3-alkylpyrroles and squaric acid showed broad and bathochromically shifted absorption in the UV-Vis spectra, compared to the spectra of the copolymers obtained from N-alkylpyrroles and squaric acid. For example, 3-DDP-co-SQA (**16b**) obtained in acetic acid/DMSO mixture had a very broad absorption stretching to the NIR region, with an absorption maximum at 639 nm in DMSO (Figure 10), whereas N-DDP-co-SQA (**13**) prepared under identical conditions showed a λ_{max} at 612 nm with a blue shift of nearly 27 nm. The UV-Vis absorption spectra of the polymer **16b** showed nearly 75 nm red shift compared to the absorption maximum (564 nm) of the squaraine dye **20** (Figure 11). The absorption maxima of different polysquaraines and their model compounds prepared under different experimental conditions are compared in Table 4, which reveal that solvents used for their preparation have

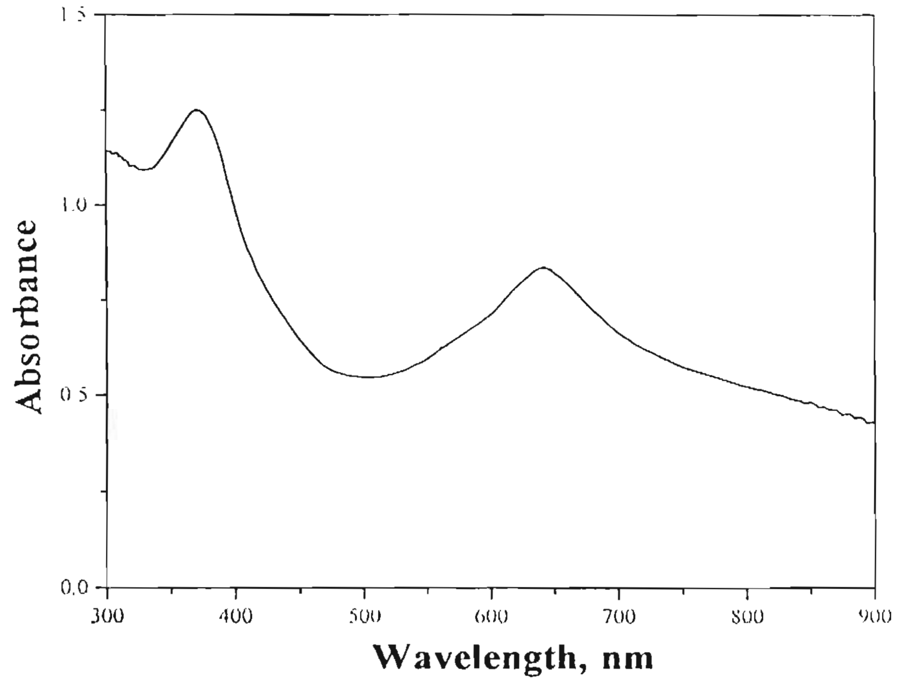


Figure 10. UV-Vis absorption spectrum of model compound **16b** in DMSO

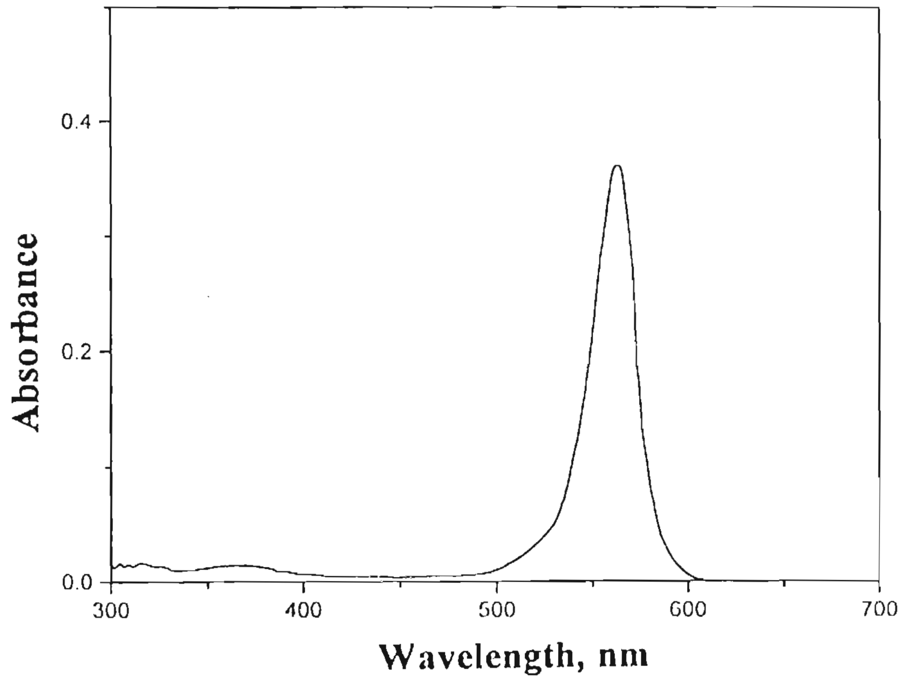


Figure 11. UV-Vis absorption spectrum of model compound **20** in DMSO.

Table 4. UV-Vis spectral data of the various polysquaraines and their model compounds

Polymers/model compounds	λ_{max} in CHCl$_3$ (nm)	λ_{max} in DMSO (nm)
N-DDP-co-SQA (**11b**)	586	606
N-DDP-co-SQA (**13**)	596	612
N-HDP-co-SQA (**11c**)	577	601
3-DDP-co-SQA (**14b**)	571	604
3-DDP-co-SQA (**15b**)	612	623
3-DDP-co-SQA (**16b**)	631	639
19	580	583
20	554	564

large influence on absorption properties. This can be attributed to the difference in conjugation length and the structure of the polymers associated with the orientational effect of squaric acid towards various pyrrole monomers during polycondensation in various solvents to form the isomeric 1,3-oriented zwitterionic and the 1,2-oriented diketonic moieties.

2.2.4.4. Solvatochromism of polysquaraines and their model compounds

The changes in the electronic absorption spectra of organic or inorganic compounds induced by the solvent polarity is referred to as solvatochromism.[39] In general, dye molecules with a large change in their permanent dipole moment upon excitation exhibit a strong solvatochromism. Several such dyes have been used to establish empirical scales of solvent polarity by means of UV-Vis-NIR spectroscopic measurements in solution.[40] The polar betaine structures of squaraine dyes are capable of inducing large changes to their electronic absorption spectra in solvents having different polarity and dielectric constant. The negative solvatochromic behaviour of squaraine dyes and their contribution to the nonlinear optical properties have been recently reported.[41,42] In order to study the solvatochromism of the new copolymers, detailed measurements of their UV-Vis absorption spectra in solvents of varying polarity were carried out. These results are listed in Table 5. The solvatochromic behaviour of organic molecules in various solvents can be related to their structural characteristics. For example, it is known in the literature that organic dyes with zwitterionic (betaine) structures show negative solvatochromism, whereas π-conjugated molecules having strong donor and acceptor groups show positive solvatochromism.[40] Therefore, the solvatochromic behaviour of polysquaraines, prepared using various solvent media, may give insight into their structural identity. In order to prove this, the absorption maxima of the polymers **11b** and **13** were measured in solvents having different polarities and the data are compared with those of the model squaraine dye **19** (Table 5).

Table 5. Absorption spectra of the polysquaraines **11b** and **13** and the model squaraine dye **19** in different solvents.

Solvent	**19** (λ_{max})	N-DDP-co-SQA (**11b**) (λ_{max})	N-DDP-co-SQA (**13**) (λ_{max})
C_6H_6	585	606	600
CCl_4	584	592	595
$CHCl_3$	580	586	596
CH_3COCH_3	577	581	604
CH_3OH	571	562	600

The polymer **11b** showed a negative solvatochromic effect as in the case of the model dye **19.** This observation indicates that **11b** has a zwitterionic structure as in the case of **19**. However, it was observed that the extent of the shift in the λ_{max} with solvent polarity was higher for **11b** (32 nm) when compared to that of **19**. This could be due to the extensive conjugation in **11b** due to its macromolecular structure when compared to the less conjugated model dye **19**. Interestingly, the solvatochromic behaviour of **13** was different from that of **11b** and showed a slight increase in the absorption maximum with increase in solvent polarity. This positive solvatochromism is in accordance with its expected structure in which considerable amount of the diketonic repeat units is also present along with the zwitterionic repeat units.

The observed negative shift in the absorption bands of the copolymers with a high content of the 1,3-zwitterionic repeat unit could be rationalized in terms of the stabilization of the ionic charges between the adjacent pyrrole and cyclobutene moieties. This indicates a decrease of the solute dipole moment upon excitation ($\mu_g > \mu_e$) and is a characteristic property of compounds with ground state inter- or intramolecular charge-transfer (CT) absorptions.[39,40] Therefore, the observed negative solvatochromism is a clear evidence for the ground state intramolecular CT in polysquaraines with 1,3-zwitterionic repeat units. On the other hand, copolymers having a high percentage of the 1,2 diketonic repeat units exhibit a bathochromic (red) shift, with increase in solvent polarity, which implies that the solute dipole moment increases during the electronic transition ($\mu_g < \mu_e$).

In alcoholic, hydrogen bonding donor (HBD) solvents, the polymers **11b** and **13** and the model dye **19** showed unique solvatochromic behaviour as indicated in Table 6. For instance, in the case of N-DPP-co-SQA (**11b**) with a high content of the 1,3-zwitterionic repeat units, a distinct hypsochromic shift is noticed in the order, 1-BuOH (578 nm) > 2-PrOH (571 nm) > EtOH (565 nm) > MeOH (562 nm), which can be explained on the basis of the ability of these solvents to form hydrogen bonded complex with **11b**. The model compound **19** showed the same trend as that of **11b**, but to a lesser extent. However, **13** with a high content of the 1,2-diketonic repeat units did not show any significant change in the absorption maxima in HBD solvents. These observations reveal that the extent of conjugation and structure of the repeat units significantly influence the solvatochromic properties of the squaraine polymers. The large shift observed in the case of N-DPP-co-SQA (**11b**) with a high percentage of the zwitterionic repeat units compared to its model compound **19** could be explained on the basis of the large conformational changes (planar/non planar) associated with the conjugated polymer backbone due to the solvent solute hydrogen bonding interaction. The observed solvatochromic behaviour also reveals that in addition to the dipole moment change on excitation, the ability of a solute to participate in hydrogen bonding with surrounding solvent molecules, in its ground or Franck-Condon excited state significantly influences the extent of solvatochromism.[43-45]

Table 6. UV-Vis absorption spectra of the polymers **11b**, **13** and the model compound **19** in alcoholic solvents.

Solvent	**19** (λ_{max})	N-DDP-co-SQA (**11b**) (λ_{max})	N-DDP-co-SQA (**13**) (λ_{max})
MeOH	571	562	600
EtOH	573	565	600
2-Propanol	574	571	600
1-Butanol	575	578	600

A plot of the absorption maxima in wave numbers (cm^{-1}) of the polymers **11b** and **13** and the model dye **19** in alcoholic hydrogen bonding solvents against their acidity parameters[46] are shown in Figure 12. The linear increase in absorption maxima observed is comparable for the polymer **11b** and the model dye **19**. On the other hand no change in the absorption maximum could be noticed for the

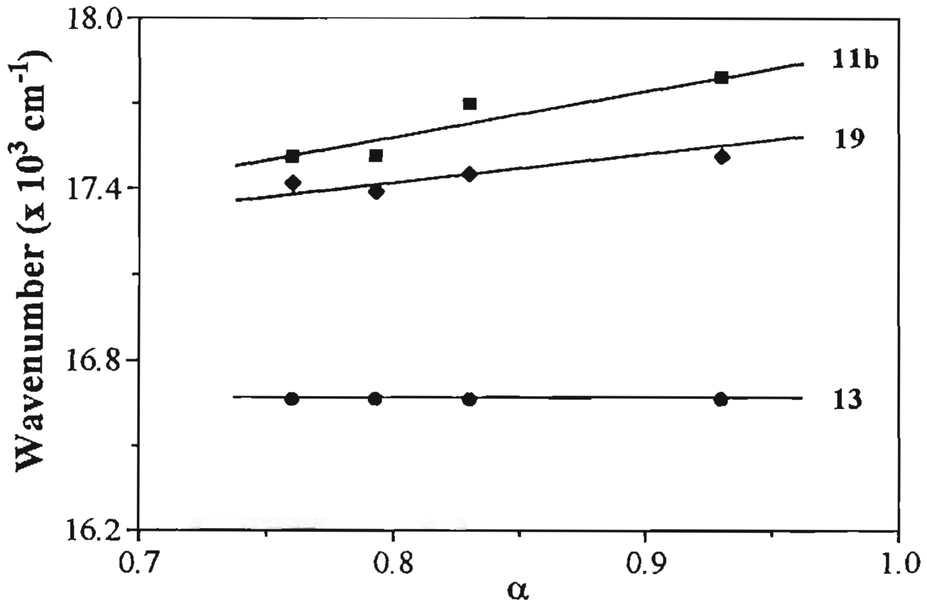


Figure 12. Plot of the absorption maxima of **11b**, **13** and **19** versus the solvent acidity parameter.

polymer **13**. Thus, the structure of the polymer repeat units play a significant role in controlling its solvatochromic behaviour. The solvatochromic properties for copolymers of 3-dodecylpyrrole and squaric acid followed the same trend as in the case of the copolymers of N-dodecylpyrrole and squaric acid and are in accordance with their proposed structures.

2.2.4.5. pH-Dependent changes of the UV-Vis absorption spectra of squaraine polymers

The squaraine polymers and model compounds prepared under different experimental conditions showed significant difference in their UV-Vis absorption spectra with changes in pH of the medium. In all cases, the intensity of the long wavelength absorption decreased with the addition of a base such as NaOH or

Et_3N in DMSO solution. Interestingly, addition of acids to the same solution brought back the original absorption and the process is reversible without any decomposition of the compounds.

The changes in the UV-Vis absorption spectra of the model compound **19** in DMSO upon addition of 0.1 N NaOH is shown in Figure 13. The intensity of the long wavelength absorption maximum at 583 nm decreased with a slight red shift on slow addition of 0.1 N NaOH. On addition of 0.1 N HCl, the violet-blue colour of the dye was regained to its original intensity, indicating that the change is reversible in acid-base media. On the other hand, the polymers **11a,b** and **14a,b** having 1,3-zwitterionic structures analogous to that of **19** showed unique spectral changes upon addition of base. The base-induced spectral changes for the polymer **11b** are as shown in Figure 14. When aqueous NaOH (0.1 M) solution was added to a solution of **11b** in DMSO, the initial bluish-green colour (λ_{max}, 606 nm) gradually decreased with the slow formation of a very broad band at the NIR region. On continuous addition of base, the 606 nm absorption further decreased with the formation of a new band around 806 nm. When aqueous HCl was added dropwise to the same solution, the initial colour was regained to its original intensity, indicating no decomposition of the polymeric dye. Thus, with change in pH of the medium, unique reversible optical changes could be noticed for all squaraine polymers having zwitterionic repeat units, which are prepared in 1-butanol/benzene medium. However, these changes could not be observed in the case of the polymers **13** and **16a,b** with a high content of the 1,2-diketonic repeat units.

Even though the structural changes associated with the pH-dependent reversible optical shift are not very clear, it could be assumed as due to the base or acid induced structural relaxations of the zwitterionic polymer repeat units,

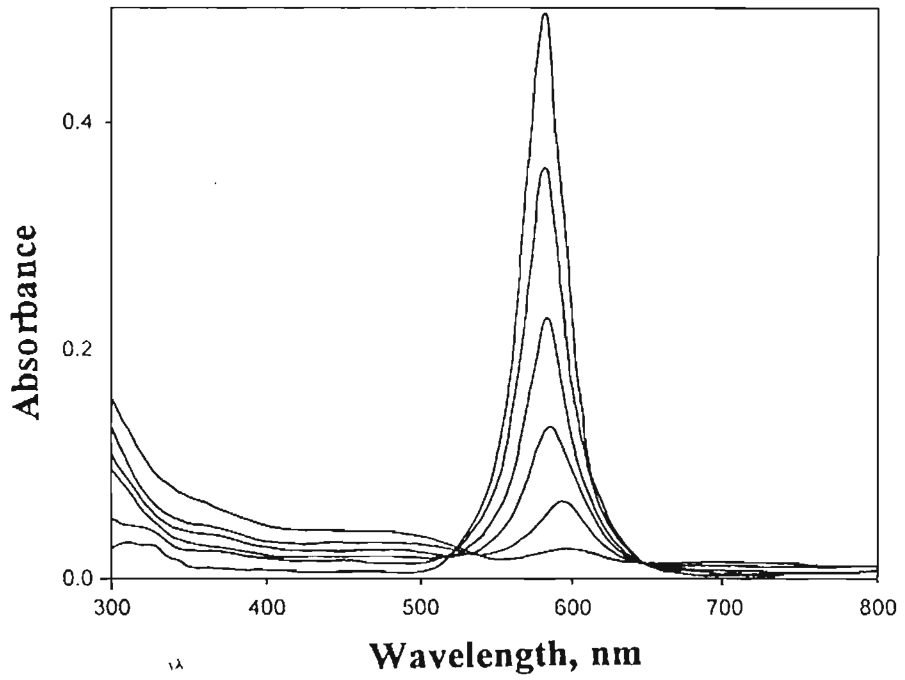
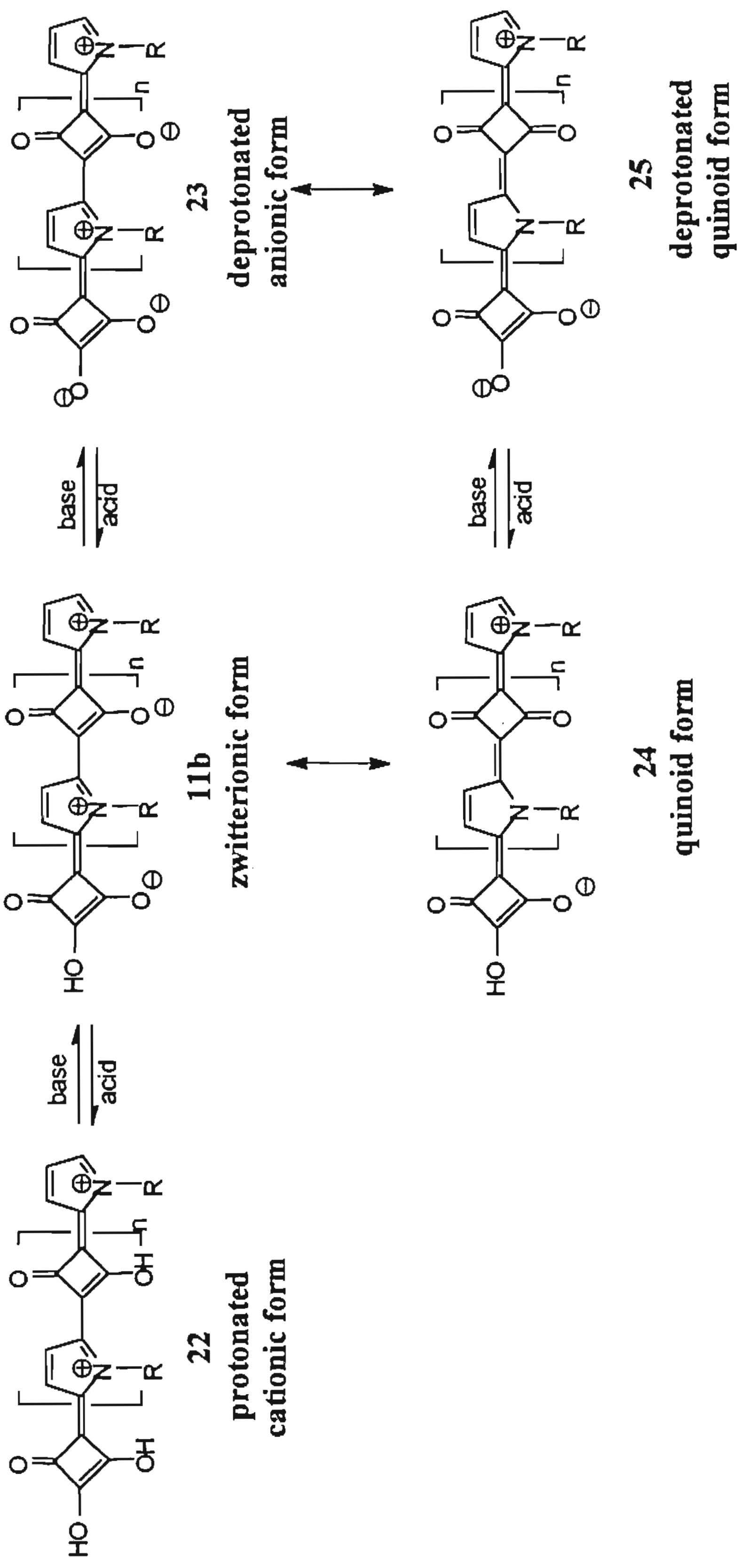


Figure 13. pH induced spectral changes of **19** in DMSO on addition of aqueous NaOH (0.1 N).

their protonated cationic form (non-polar) and deprotonated anionic form (planar) as indicated in Scheme 12. In acids or in protic solvents, the polymer **11b** may be in its protonated cationic form **22** rather than the original zwitterionic structure. On addition of base, deprotonation occurs bringing back the polymer to its zwitterionic form **11b** and the mesomeric quinoid form **24**. On further addition of base, a second deprotonation occurs and the polymer changes to its deprotonated anionic form **23** which can be resonance stabilized to its deprotonated quinoid form **25**.



22
protonated cationic form

11b
zwitterionic form

23
deprotonated anionic form

24
quinoid form

25
deprotonated quinoid form

Scheme 12

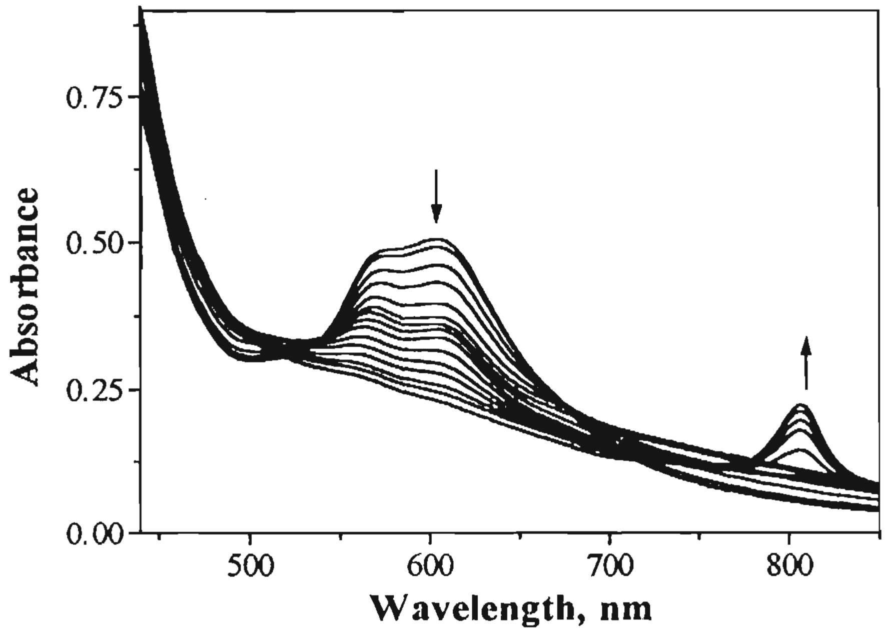


Figure 14. pH induced spectral changes of **11b** in DMSO on addition of aqueous NaOH (0.1 N).

2.2.5. Solid state properties

2.2.5.1. X-ray diffraction studies

The X-ray diffraction patterns of the conjugated polymers in the powder or film form provide insight into their structural ordering at the microscopic level. This has been well-established in the case of several π-conjugated polymers, particularly in the case of several polythiophenes.[47-49]

X-ray diffraction patterns of the solution cast films of all polysquaraines showed partially crystalline, self-organized lamellar morphology with three-dimensional ordering of the polymer chains. For example, the X-ray diffraction patterns of N-DDP-co-SQA (**11b**) and 3-DDP-co-SQA (**15b**) films, which were cast from chloroform solutions showed strong first order reflections at 2θ angle of 4.8° and 4.9°, respectively (Figure 15). These values correspond to an interlayer d-spacing of 18.32 Å and 17.98 Å, respectively which are characteristic of the well-organized lamellar assemblies similar to those of poly(3-alkylthiophenes).[50] However, this interlayer distance in polysquaraines are relatively smaller in comparison to those of polypyrroles or polythiophenes, containing the same alkyl chains. This close packing could be due to the strong dipolar interactions among the 1,3-zwitterionic groups. In addition to this, in squaraine copolymers there are less steric repulsions among the alkyl chains due to the presence of the cyclobutene spacer moiety between two pyrrole groups which allows more close packing of the polymer chains.

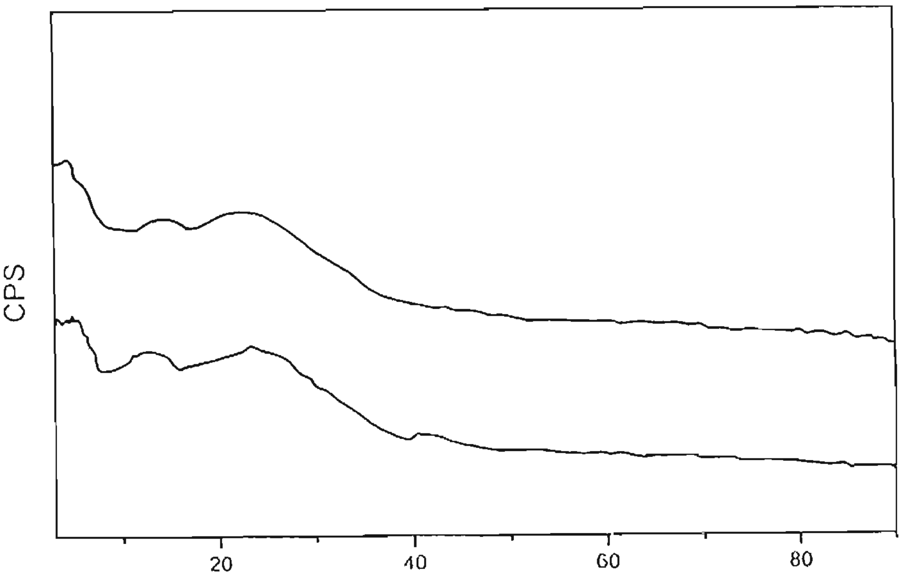


Figure 15. X-diffraction patterns of (a) **11b** and (b) **15b**.

The X-ray diffraction patterns also reveal that the interlayer spacing between polymer chains depends upon the length of the alkyl side chain. With the elongation of the alkyl side chain, the first order reflection angle 2θ decreases and the corresponding interlayer spacing increases. For example, the d-spacing of a polysquaraine obtained by the condensation of N-methylpyrrole and squaric acid is approximately 6.9 Å and that of **11a** and **11b** having octyl and dodecyl side chains are 17.17 Å and 18.32 Å, respectively. In the case of polymers with long alkyl side chains, a broad diffraction centered around 20-25° corresponding to an interlayer spacing of 4.4-3.5 Å could also be observed. This was particularly significant in the case of polymers **13** and **16a,b** with a high percentage of the 1,2-diketonic repeat units. The broad diffraction at this wide angle area can be attributed to the disruption of stacking due to a disordered phase associated with the 1,2-diketonic units of the polymers. In general, the X-ray diffraction patterns reveal that the polysquaraines with long alkyl side chains are not completely amorphous but a combination of partially ordered and disordered conformations as indicated in Figures 16 and 17.

2.2.5.2. Thermogravimetric analysis (TGA)

Polymers prepared under different experimental conditions respond differently during thermal analysis. TGA patterns of some representative copolymers under air are shown in Figure 18. Polymers with a high percentage of the 1,3-zwitterionic repeat units showed better thermal stability over those with high content of the 1,2-diketonic repeat units. In air, at a heating rate of 20 °C/min, all copolymers showed considerable thermal stability up to 200 °C. All the

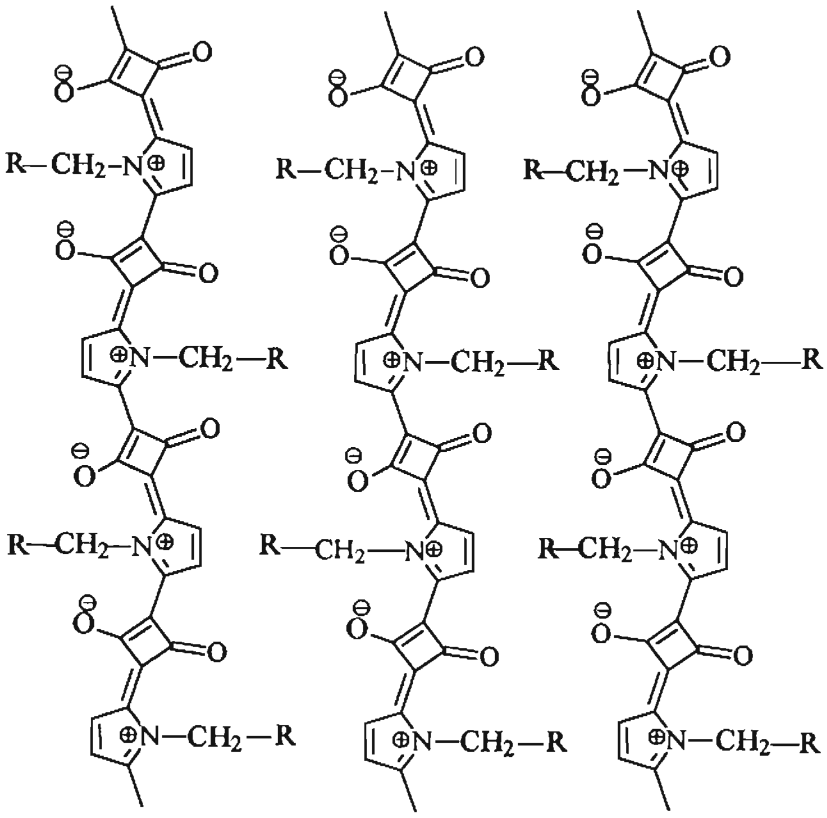


Figure 16

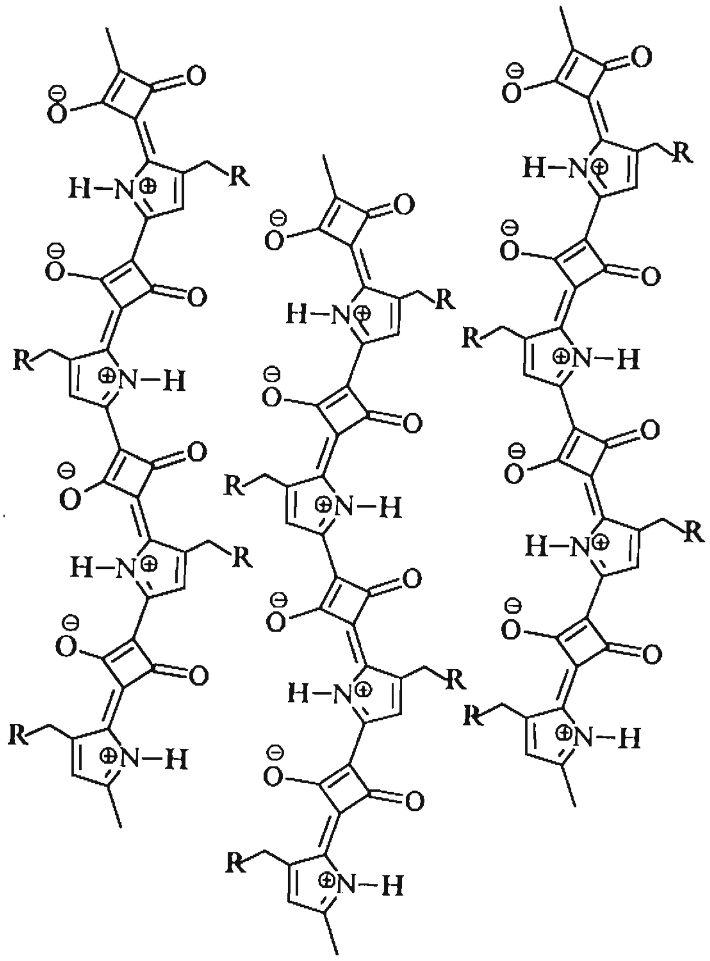


Figure 17

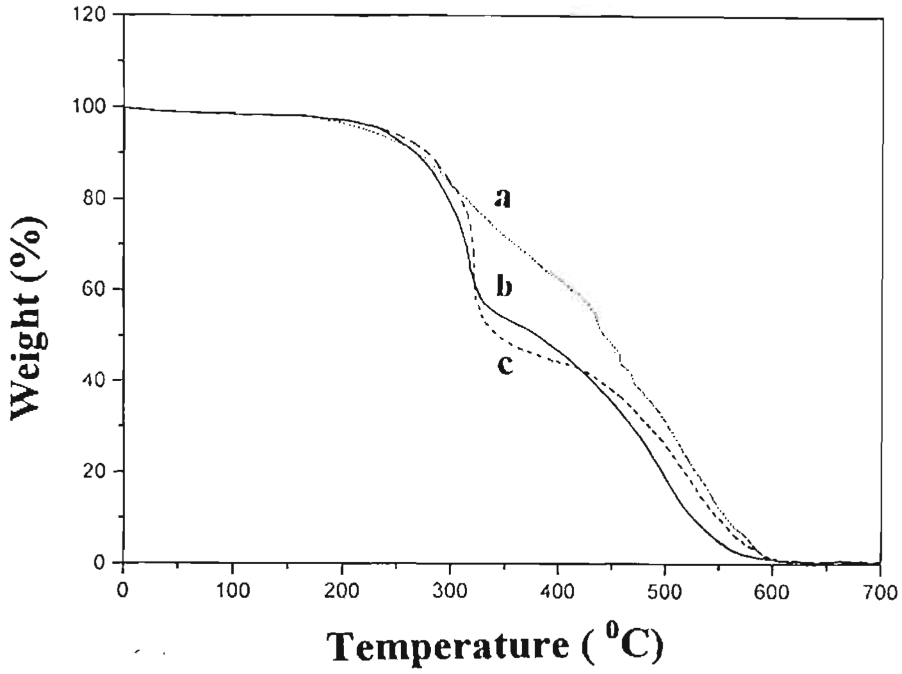


Figure 18. TGA of polymers (a) **11b** (b) **13** and (c) **12**.

polysquaraines under investigation showed sharp weight loss around 300 °C, probably due to the degradation of the alkyl chains. A second weight loss was also noticed around 500 °C which could be due to the polymer backbone degradation.

2.2.5.3. Solid state UV-Vis-NIR spectral studies

Information on the solid state properties, such as electronic transitions, bandgaps and aggregation (ordering) of polymeric materials can be obtained from their solid state electronic absorption spectra. In most cases, solid state electronic absorption spectra of π-conjugated polymers are different from their solution spectra. In many cases broad and bathochromically shifted spectra are obtained for polymer films due to enhanced coplanarity of the polymer backbone or due to solid state aggregation/ordering.

The solid state UV-Vis spectra of squraine dyes in general are known to show large red shift (panchromatic shift) to the NIR region due the crystal packing in the solid state. However, the solid state UV-Vis spectra of the new squaraine polymer films did not show any significant change when compared to those of model squaraine dyes. On the other hand, the solid state spectral features of polymers prepared under different experimental conditions were different as in the

Table 8. Electronic absorption maxima, absorption edge (onset), and bandgaps of various polysquaraines and their model compounds

No.	Polymer/model compounds	Absorption maximum, (nm)	Absorption edge, (nm)	Eg (eV)
1	N-DDP-co-SQA (**11b**)	606	800	1.55
2	N-DDP-co-SQA (**13**)	612	800	1.55
3	3-DDP-co-SQA (**14b**)	604	780	1.59
4	3-DDP-co-SQA (**15b**)	633	1100	1.13
5	3-DDP-co-SQA (**16b**)	645	1100	1.13
6	**19**	583	660	1.78
7	**20**	564	610	2.03

case of their solution UV-Vis spectra. The solid state UV-Vis-NIR spectra of a few representative polysquaraines are presented in Figures 19. The solid state spectrum of the polymer **16b** prepared in acetic acid/DMSO showed the maximum absorption for the π-π^* transition at 645 nm with a shoulder around 845 nm (Figure 19, a), whereas the corresponding spectra for the polymer **11b** prepared in 1-butanol showed the maximum absorption at 633 nm with a shoulder around 840 nm (Figure 19, b). In both the cases the solid state absorption spectra were tailing beyond 1100 nm. The absorption beyond 1100 nm could not be recorded with the spectrometer used in this study. Therefore, the actual bandgap of the polymers, which are usually obtained from the onset of absorption, could not be calculated in these cases. Nevertheless, the bandgap of the polymers calculated using 1100 nm

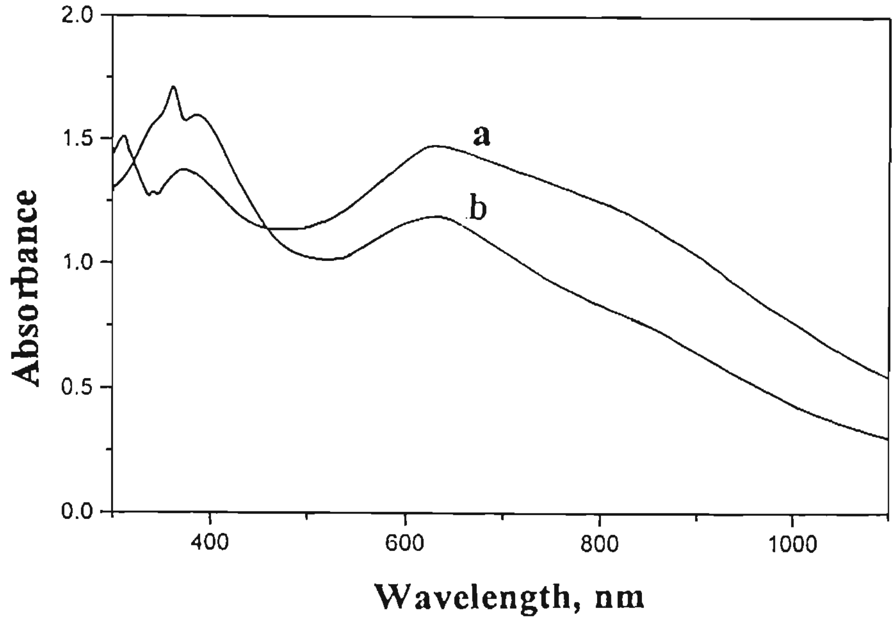


Figure 19. Solid state UV-Vis absorption spectra of polymers (a) **11b** and (b) **16b**

as the onset of absorption is 1.13 eV. The lowest energy absorption maxima (λ_{max}), the onset of absorption edges, and the corresponding bandgaps of the different copolymers under investigation and of their model compounds are summarized in Table 8. The polymers prepared in acetic acid-DMSO mixture had longer conjugation length than the polymers obtained in 1-butanol-benzene as evidenced from their low Eg. The band gap of 1.13 eV is a relatively low value compared to the Eg of many polypyrroles and polythiophenes. Similarly, the optical bandgap of the copolymers are very low compared to the model squaraine dye **19** (optical bandgap, 2.03 eV). This observation further supports the recent theoretical predictions of the low bandgap energy for polysquaraines.[31,32]

2.2.5.4. Electrical conductivity

The electrical conductivites of the different polysquaraines were measured by the standard four-probe method using pressed pellets at room temperature. The electrical conductivities of the undoped polymers significantly change with their structure (Table 9). For example, the conductivities of the polysquaraines obtained from 1-butanol-benzene mixture under reflux conditions are found to be in the range of 10^{-7} S/cm. This is obvious from its solid state absorption spectrum and the calculated bandgap energy. The polymers obtained in DMSO-acetic acid showed higher conductivities in the range of 10^{-4} S/cm due to their better conjugation, as evidenced by their optical absorption spectra and bandgap energies. Even though the conductivities of the virgin samples are taken as the undoped conductivity, the possibility of oxidative doping of the polymer backbone by air and light during handling cannot be ruled out.

The effect of various dopants on conductivity is listed in Table 10. On doping with iodine, the conductivities of all the polymers under investigation enhanced significantly and up to about 10^{-4} S/cm. Similarly, doping with other dopants such as 4-toluenesulfonic acid and $FeCl_3$ also significantly enhanced the conductivity. The increase in conductivity on doping could be due to the formation of polarons and bipolarons which enhance the charge carrier mobility of the polymers. Increase in the alkyl chain length of the copolymers slightly decreased their conductivity probably due to the enhanced interlayer separation, which may

Table 9. Electrical conductivity values of the squaraine copolymers prepared under different conditions.

Polymer	Experimental conditions	Undoped conductivity (S/cm)	I_2 doped conductivity (S/cm)
N-OCP-co-SQA (**11a**)	1-butanol/benzene, 12 h reflux	3.25×10^{-6}	3.4×10^{-4}
N-DDP-co-SQA (**11b**)	1-butanol/benzene, 12 h reflux	1.26×10^{-7}	2.5×10^{-4}
N-DDP-co-SQA (**13**)	AcOH/DMSO, 6 days, 30 °C	2.5×10^{-6}	1×10^{-3}
N-HDP-co-SQA (**11c**)	1-butanol/benzene, 12 h reflux	1×10^{-7}	1.1×10^{-5}
3-OCP-co-SQA (**14a**)	1-butanol/benzene, 12 h, reflux	8×10^{-6}	6.0×10^{-4}
3-DDP-co-SQA (**15b**)	1-butanol/Ac_2O, 48 h, 30 °C	6×10^{-5}	3.2×10^{-3}
3-DDP-co-SQA (**16b**)	AcOH/DMSO, 48 h, 30 °C	2.3×10^{-4}	1.8×10^{-2}

reduce the efficiency of interlayer electron hoping which enhance the charge carrier mobility of the polymers.

Table 10. Electrical conductivity values of N-DDP-CO-SQA(**11b**) with different dopants

Dopant	Specific conductivity (S/cm)
Undoped	1.26×10^{-7}
Iodine	2.5×10^{-4}
4-Toluenesulfonic acid	6.4×10^{-4}
Ferric chloride	5.0×10^{-3}

2.3. Conclusions

Condensation copolymerization of squaric acid with N-alkyl- or 3-alkylpyrroles gave a series of conjugated copolymers containing 1,3-zwitterionic and 1,2-diketonic repeat units. The solvents employed for the polycondensation are found to have profound influence on controlling the orientation of the pyrrole moieties on the cyclobutene ring. The molecular weight, solubility, optical and electronic properties of the squaraine copolymers are significantly influenced by the presence of the 1,2-oriented diketonic repeat units. Copolymers with high content of the 1,2-diketonic repeat units have better solubility and molecular weight. They showed low bandgap energies and better intrinsic conductivities compared to those of polymers with a high percentage of the zwitterionic repeat units.

2.4. Experimental Section

All melting points are uncorrected and were determined using a Mel-Temp-II melting point apparatus. The IR spectra were recorded on a Perkin Elmer model 882 Infrared spectrometer. The electronic absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer or Shimadzu UV-160A Spectrophotometer or on a GBC double beam UV-Visible spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a JEOL EX 90, NMR spectrometer using tetramethyl-silane (TMS) as internal standard. The mass spectra were recorded on a Hewlett Packard mass spectrometer model 5791, attached to 5890 series II gas chromatography setup, attached with an OV 101 (25 m length, 0.2 mm ID) or on MP-FFAP (25 m length, 0.2 mm ID) capillary column, and an FID detector. Thermogravimetric analyses (TGA) were carried out on a V5.1A Dupont 2000 TGA analyser. .X-ray diffractions (XRD) were obtained on a Rigaku (Japan) X-ray Diffractometer (CuKα, = 1.5406 Å, Ni filter). Elemental analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. The molecular weights were determined by gel permeation chromatography (GPC) using polystyrene standards on a Shimadzu LC4A. Tetrahydrofuran was used as the eluent at a flow rate of 1 mL min^{-1} at 28 °C. The conductivities of the polymers were measured by the standard four point probe method on pressed pellets.

Pyrrole (SRL India) was distilled and kept under nitrogen atmosphere before use. N-Methylpyrrole (99%), 2,4-dimethylpyrrole (97%), squaric acid (98%), diethyl squarate (98%), 1-bromooctane (99%), 1-bromododecane (97%) and 11-bromoundecanol (98%) were purchased from Aldrich and were used without further purification. Octanoyl chloride and lauroyl chloride were prepared by the reaction of thionyl chloride with the corresponding acids. All other reagents and solvents were locally purchased and purified according to literature procedures, wherever it was necessary.

2.4.1. Preparation of starting Materials

2.4.1.1. Preparation of N-octylpyrrole (4a)

A nitrogen purged flask equipped with a reflux condenser was charged with methylene chloride (10 mL), tetrabutylammonium bromide (4.84 g, 15 mmol), pyrrole (1 g, 15 mmol) and 1-bromooctane (1.93 g, 10 mmol). The mixture was cooled to 0°C using an ice bath, followed by dropwise addition of 50% sodium hydroxide (10 mL). After addition, the reaction mixture was refluxed for 24 h. The mixture was cooled and diluted with water (5 mL), and the aqueous phase was extracted with methylene chloride (3 x 5 mL). The combined organic extracts were washed with 3 N HC1, water, and brine and dried over sodium sulfate. The solvent was removed *in vacuo*, and the crude product was purified by column chromatography (silica gel, 100-200 mesh, petroleum ether/EtOAc 9:1) to afford 1.7 g (95%) of **4a**, bp 123 ^{0}C (15 mm/Hg). IR ν_{max} (neat) 2934, 2863, 1541, 1500, 1451, 1285, 1091, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.88 (3 H, t, J = 6.9 Hz, CH_3), 1.28 (10 H, s, CH_2), 1.75 (2 H, m, CH_2), 3.83 (2 H, t, J = 7.2 Hz, N-CH_2), 6.11 (2 H, t, J = 2.1 Hz, aromatic), 6.62 (2 H, t, J = 2.1 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 13.93, 22.52, 26.67, 29.06, 31.47, 31.68, 49.46, 107.7, 120.23; Mass spectrum, m/z 179 (M^+, 15), 164 (1), 150 (3), 136 (5), 122 (9), 108 (8), 94 (13), 81 (100), 80 (43), 68 (7), 67 (8).

2.4.1.2. Preparation of 1-dodecylpyrrole (4b)

1-Dodecylpyrrole (**4b**) was synthesized by the reaction of pyrrole (**1**) and 1-bromododecane using tetrabutylammonium bromide as phase-transfer reagent as per the above mentioned procedure in a 68% yield. IR ν_{max} (neat) 3107, 2912, 2851, 1533, 1497, 1461, 1369, 1276, 1087, 1061, 964, 717 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.86 (3 H, t, J = 6.9 Hz, CH_3), 1.25 (18 H, s, CH_2), 1.73 (2 H, m, CH_2), 3.85 (2 H, t, J = 7.2 Hz, N-CH_2), 6.11 (2 H, t, J = 2.1 Hz, aromatic), 6.64 (2 H, t, J = 2.1 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.0, 22.52, 26.60, 29.22, 29.31, 29.41, 29.48, 29.58, 31.10, 31.47, 31.68, 49.46, 107.70, 120.23; Mass spectrum, m/z 235 (M^+, 11), 220 (2), 206 (2), 192 (4), 178 (3), 165 (4), 150 (5), 136 (9), 122 (12), 108 (7), 94 (15), 81 (100), 66 (8).

2.4.1.3. Preparation of 11-(1-pyrrolyl)undecanol (5)

To a solution of potassium *tert*-butoxide (5.6 g, 50 mmol) in dry diethyl ether (100 mL) was added pyrrole (3.4 g, 50 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was brought to room temperature and stirred for 2 h, followed by the addition of 18-crown-6 (1.5 g, 5.7 mmol). To this solution, 11-bromo-1-undecanol (15.18 g, 60 mmol) in dry diethyl ether (50 mL) was added dropwise and stirring was continued for 18 h. After adding water (50 mL) and saturated NaCl solution (100 mL), the organic layer was collected. The aqueous layer was further extracted with ether (2 x 50 mL) and the combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the crude product was chromatographed (silica gel, 100-200 mesh, petroleum ether/EtOAc (9:1)) to give the title compound (9 g, 76%) as a colourless liquid. IR ν_{max} (neat) 3360, 2933, 2862, 1506, 1464 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.1-1.4 (18 H, m, CH_2), 1.80 (1 H, s, D_2O exchangeable, OH), 3.60 (2 H, t, J = 13.4 Hz, CH_2OH), 3.85 (2 H, t, N-CH_2), 6.10 (2 H, t, J = 2.1 Hz, aromatic), 6.65 (2 H, t, J = 2.1 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 25.65, 26.67, 29.12, 29.30, 29.40, 29.47, 31.11, 31.47, 32.69, 49.52, 62.86, 107.67, 120.35; Mass spectrum, m/z 237 (M^+, 10), 220(2), 136 (7), 122 (100), 94 (13), 81 (11), 66

(10); Anal. calcd. for $C_{15}H_{27}NO$: C, 75.90; H, 11.46; N, 5.9. Found: C, 75.93; H, 11.45; N, 5.94.

2.4.1.4. Preparation of 1-(phenylsulfonyl)pyrrole (6)

This compound was prepared by the reaction of pyrrole (**1**) and benzenesulfonyl chloride using tetrabutylammonium hydrogensulfate as phase transfer catalyst according to reported procedures[36-37] in a 75% yield, mp 87-88 ^{0}C. IR ν_{max} (KBr) 3172, 1519, 1539, 1456, 1371, 1173, 1059 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 6.3 (2 H, t, aromatic), 7.2 (2 H, t, aromatic), 7.45-7.75 (3 H, m, aromatic), 7.8-7.95 (2 H, m, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 113.61, 120.68, 126.59, 129.24, 133.72, 138.9; Mass spectrum m/z 207 (M^+, 93), 155 (60), 91 (100), 65 (15).

2.4.1.5. Preparation of 1-[(1-phenylsulfonyl)-3-pyrrolyl]-1-octanone (7a)

To a suspension of anhydrous $AlCl_3$ (2.67 g, 20 mmol) in 50 mL of dichloromethane at 25 °C was slowly added octanoyl chloride (3 g, 18.4 mmol) and the resulting solution was stirred at 25 °C for 10 min. To this a solution of 1-(phenylsulfonyl)pyrrole (3.3 g, 16 mmol) in 10 mL of dichloromethane was added slowly, and the mixture was stirred at 25 °C for 90 min. The reaction was quenched with ice and water, and the product was extracted with dichloromethane. Removal of the solvent followed by column chromatography (silica gel, 100-200 mesh) of the residue, and eluting with 10% petroleum ether/ethyl acetate, gave 4.75 g (77%) of **7a**. IR ν_{max} (neat) 3141, 2929, 2865, 1739, 1682, 1544, 1483, 1381, 1287, 1181, 1092 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.85 (3 H, t, CH_3), 1.1-1.8 (10 H, m, CH_2), 2.75 (2 H, t, $COCH_2$), 6.6-6.75 (1 H, m, aromatic), 7.15 (1 H, t, aromatic), 7.45-7.65 (3 H, m, aromatic), 7.75 (1 H, t, aromatic), 7.85-7.95 (2 H, m, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 13.90, 22.46, 24.22, 28.95, 29.15, 31.53, 39.68, 112.44, 121.45, 124.02,. 127.0, 129.18, 129.57, 134.43, 195.53; Mass spectrum m/z 333 (M^+, 2), 249 (26), 234 (15), 192 (5), 141 (25), 94 (11), 77 (100), 66 (5).

2.4.1.6. Preparation of 1-(1-phenylsulfonyl)-3-pyrrolyl-1-dodecanone (7b)

Compound **7b** was synthesized as per the same procedure described for **7a**, in a 82% yield, mp 49-50 °C. IR ν_{max} (KBr) 3147, 2935, 2861, 1680, 1548, 1488, 1456, 1388, 1338, 1285, 1184, 1128, 1099, 805, 755 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.85 (3 H, t, CH_3), 1.15-1.85 (18 H, m, CH_2), 2.75 (2 H, t, $COCH_2$), 6.6-6.75 (1 H, m, aromatic), 7.15 (1 H, t, aromatic), 7.45-7.65 (3 H, m, aromatic), 7.75 (1 H, t, aromatic), 7.85-7.95 (2 H, m, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.02, 22.58, 24.28, 29.26, 29.41, 29.53, 31.83, 39.74, 112.50, 121.48, 124.05, 127.06, 129.21, 129.63, 134.46, 138.19, 195.53; Mass spectrum m/z 389(M^+, 3), 305 (25), 291 (15), 277 (20), 249 (24), 234 (17), 192 (6), 141 (27), 94 (12), 77 (100), 66 (5).

2.4.1.7. Preparation of 3-octylpyrrole (8a)

1-[1-Phenylsulfonyl)-3-pyrrolyl]-1-octanone (**7a**) (0.5 g, 1.5 mmol) was dissolved in toluene (20 mL). Water (8 mL) and amalgamated zinc (12 g) were added, followed by the addition of concentrated HCl (20 mL). The reaction mixture was heated under gentle reflux with stirring for 25 h. After cooling, the organic layer was separated and the aqueous layer was extracted with toluene. The combined organic layers were evaporated under reduced pressure and the crude product was stirred with aqueous NaOH (5 N, 5 mL) and 2-propanol (7 mL) under reflux for 6 h. After cooling, 2-propanol was removed under reduced pressure and the aqueous residue was extracted with ether (3 x 20 mL). The organic fraction was washed with brine, dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (100-200 mesh) using a mixture (9.5:0.5) of petroleum ether and ethyl acetate to give 0.15 g (84%) of **8a**. IR ν_{max} (neat) 3409, 2931, 2859, 1671, 1564, 1465, 1064 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.85 (3 H, t, J = 10.7 Hz, CH_3;) 1.15 - 1.65 (12 H, m, CH_2), 2.48 (2 H, t, J = 7.6 Hz, CH_2), 6.05-6.15 (1 H, m, aromatic), 6.55-6.65 (1 H, m, aromatic), 6.6-6.75 (1 H, m, aromatic), 7.65-8.2 (1 H, br, s, NH); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.02, 22.64, 26.91, 29.29, 29.50, 31.20, 31.89, 33.23, 108.45, 114.77, 117.49, 124.56; Mass spectrum m/z 179 (M^+, 22), 164 (2), 150 (2), 136 (3), 122 (3), 94 (20), 80 (100), 67 (4).

2.4.1.8. Preparation of 3-dodecylpyrrole (8b)

To a 1 L, three necked flask, fitted with a thermometer, a condenser, an argon inlet and a 150 mL funnel, 1.93 g of lithium aluminum hydride (50 mmol) and 60 mL of THF (dry) were introduced. A solution of **7b** (3.9 g, 10 mmol) in 100 mL of dry THF was slowly added. The mixture was refluxed for 1.5 h, cooled and quenched slowly under argon with brine. The resulting residue was filtered, washed with THF, and the combined organic layer was concentrated under reduced pressure to give 3 g (80%) of the reduced product. To this residue, 2-propanol (70 mL) was added and refluxed with 50 mL of 5 N aqueous NaOH for 8 h. After cooling to room temperature, 2-propanol was removed under reduced pressure and the aqueous layer was extracted with ether (3 x 10 mL). The combined ether extracts were washed with water, dried over anhydrous sodium sulfate and concentrated to give 1.5 g (68%) of the title compound as a colourless liquid. IR ν_{max} (neat) 3404, 2928, 2861, 1678, 1567, 1466, 1066 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.87 (3 H, t, J = 10.7 Hz, CH_3), 1.26 (20 H, m, CH_2) 2.48 (2 H, t, J = 7.6 Hz, CH_2) 6.08 (1 H, m, aromatic) 6.53 (1 H, m, aromatic), 6.65 (1 H, t, J = 2.2 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.08, 22.70, 26.97, 29.38, 29.59, 29.71, 31.26, 31.95, 108.57, 114.80, 117.55, 124.66; Mass spectrum, m/z 221 (M^+,22), 207 (2), 193 (3), 179 (4), 164 (4), 150 (2), 136 (3), 122 (2), 94 (20), 80 (100), 67 (4).

2.4.1.9. Preparation of 1-dodecyl-2,4-dimethylpyrrole (10)

To a suspension of 300 mg of 18-crown-6 in 30 mL of dry ether was added 1.12 g (10 mmol) of potassium *tert*-butoxide. To this 10 mmol (0.95 g) of 2,4-dimethylpyrrole was introduced in a single portion with stirring and the stirring was continued for 2 h. 1-Bromododecane (2.5 g, 10 mmol) was then added dropwise to the reaction mixture. The reaction vessel was then stoppered and stirring was continued for 18 h. The reaction mixture was filtered and the inorganic salts were washed with ether (2 x 25 mL). The combined organic layer was treated with 150 mL of saturated sodium chloride and then dried over anhydrous sodium sulfate. The solvent was removed and the crude product was purified by column chromatography [silica gel (100-200 mesh), hexane/ethyl acetate (9:1)] to give 1.5 g (57%) of the title compound as an yellow liquid. IR ν_{max} (neat) 2931, 2861, 1701, 1678, 1570, 1533, 1510, 1471, 1377, 1265, 952, 719 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.88 (3 H, t, CH_3), 1.03-1.43 (20 H, m, CH_2), 2.04 (3 H, s, CH_3), 2.16 (3 H, s, CH_3), 3.39 (2 H, s, NCH_2), 5.69 (1 H, s, aromatic), 6.31 (1 H, s, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 11.75, 11.81, 14.08, 22.67, 26.85, 28.22, 28.79, 29.32, 29.62, 31.47, 31.92, 32.87, 33.80, 46.36, 107.91, 117.55, 127.96, 129.50; Mass spectrum m/z: 263 (M^+, 5), 249 (4), 192 (3), 179 (4), 150 (6), 122 (24), 100 (100), 94 (20), 67 (9).

2.4.2. Preparation of polymers of N-substituted pyrroles and squaric Acid

2.4.2.1. Preparation of poly (1-octylpyrrole-co-squaric acid) (11a)

A flask equipped with an azeotropic reflux condenser was charged with 1-butanol (20 mL), benzene (10 mL), N-octylpyrrole (**4a**) (0.89 g, 5 mmol) and squaric acid (**2**) (0.57 g, 5 mmol) under nitrogen atmosphere. The reaction mixture was stirred and refluxed for 12 h with azeotropic removal of water. The dark blue viscous solution obtained was filtered and the filtrate was collected and concentrated under *vacuo*. The thick paste of the crude product was poured into diethyl ether. The precipitate obtained was collected by filtration, redissolved in chloroform and reprecipitated from diethyl ether to give 0.8 g (58%) of **11b**. IR ν_{max} (KBr) 2961, 2931, 2860, 1732, 1628, 1561, 1486, 1358, 1081 cm^{-1}; UV λ_{max} ($CHCl_3$) 561 nm, (1-butanol) 558 nm (DMF) 567 nm; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.85 (3 H, br, s, CH_3), 1.22 (14 H, br, s, CH_2), 2.9-3.4 (2 H, br, s, CH_2); Anal. calcd for $(C_{16}H_{19}NO_2)_n$: C, 74.70; H, 7.39; N, 5.44. Found: C, 75.1; H, 7.9; N, 5.1.

2.4.2.2. Preparation of poly (1-dodecylpyrrole-co-squaric acid) (11b)

This polymer (1.05 g, 63%) was synthesized by condensing 1-dodecylpyrrole (1.18 g, 5 mmol) with squaric acid (0.57 g, 5 mmol) under the same conditions as described for **11a**. IR ν_{max} (neat) 2961, 2931, 2860, 1732, 1628, 1561, 1486, 1358, 1081 cm^{-1}; UV λ_{max} ($CHCl_3$) 586 nm, (1-butanol) 578 nm, (DMF) 614 nm; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.85 (3 H, br, s, CH_3), 1.22 (18 H, br, s, CH_2), 1.7 (2 H, br, s, CH_2), 3.38 (2 H, br, s), 4.5-4.7 (2 H, br, s); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.09, 22.66, 26.59, 29.22, 29.31, 29.40, 29.48, 29.69, 31.10, 31.89, 40.19, 108.33, 111.50, 124.54, 130.7, 167.0, 188.9; Anal. calcd for $(C_{20}H_{27}NO_2)_n$: C, 76.67; H, 8.62; N, 4.47. Found: C, 75.60; H, 9.36; N, 4.64.

2.4.2.3. Preparation of poly (11-(1-pyrrolyl)undecanol-co-squaric acid) (11c)

The title polymer (1.0 g, 60%) was synthesized by condensing 11-(1-pyrrolyl)undecanol (1.19 g, 5 mmol) with squaric acid (0.57 g, 5 mmol) under the same conditions as described for **11a.** IR ν_{max} (neat) 3434, 2932, 2859, 1770, 1600, 1582, 1414, 1360, 1071 cm^{-1}; UV λ_{max} ($CHCl_3$) 577 nm, (1-butanol) 560 nm, (DMF) 601 nm; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.3 (18 H, br, s, CH_2), 2.7 (1 H, s, OH), 3.4 (2 H, t, CH_2), 3.65 (2 H, t, CH_2), 6.5-6.7 (2 H, br, s, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 25.58, 26.66, 29.14, 29.30,. 29.40, 29.59, 31.1, 31.9, 41.0, 60.27, 110.56, 112.6, 118.4, 123.5, 125.01, 130.2, 167.0, 189.88; Anal. calcd for $(C_{19}H_{25}NO_3)_n$: C, 72.38; H, 7.93; N, 4.44. Found: C, 71.12; H, 8.58; N, 3.99.

2.4.2.4. Preparation of poly (1-dodecylpyrrole-co-squaric acid) (12)

Squaric acid (57 mg, 0.5 mmol) and 1-dodecylpyrrole (0.12 g, 0.5 mmol) were stirred for three days in a mixture of acetic anhydride (7.5 mL) and 1-butanol (7.5 mL) under nitrogen atmosphere at room temperature. The contents of the flask were cooled, filtered and the green pasty liquid was poured into water to remove the acetic anhydride. The precipitated product was washed several times with water, methanol and diethyl ether, and was dried in a vacuum oven at 40 °C for 24 h to give **12** in 60% yield. IR ν_{max} (neat) 2930, 2860, 1767, 1730, 1639, 1552, 1472, 1355, 1084 cm^{-1}; UV λ_{max} ($CHCl_3$) 596 nm, (1-butanol) 600 nm, (DMF) 604 nm; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.85 (3 H, br, s), 1.22 (18 H, br, s), 1.7 (2 H, br, s), 3.38 (2 H, br, s), 6.5-6.7 (2 H, br, s, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.05, 22.67, 26.37, 29.22, 29.32, 29.40, 29.48, 29.62, 31.10, 31.89, 40.19, 108.33, 111.50, 118.30, 123.48, 163.46, 175.16; Anal. calcd for $(C_{20}H_{27}NO_2)$n: C, 76.67; H, 8.62; N, 4.47. Found: C, 75.68; H, 9.2; N, 4.4.

2.4.2.5. Preparation of poly (1-dodecylpyrrole-co-squaric acid) (13)

Squaric acid (57 mg, 0.5 mmol) and 1-dodecylpyrrole (0.12 g, 0.5 mmol) were stirred for six days in a mixture of glacial acetic acid (7.5 mL) and DMSO (7.5 mL) under nitrogen atmosphere at room temperature. The contents of the flask were cooled, filtered and the green pasty liquid was poured into water. The precipitated product was washed several times with water, methanol and diethyl ether. The polymer was redissolved in chloroform and reprecipitated from methanol. The product **13** was obtained in a 60% yield after drying in a vacuum oven at 40 °C for 24 h. IR ν_{max} (neat) 2930, 2860, 1767, 1730, 1639, 1552, 1472, 1355, 1084 cm^{-1}; UV λ_{max} (CHCl$_3$) 596 nm, (1-butanol) 600 nm, (DMF) 604 nm; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 0.85 (3 H, br, s), 1.22 (18 H, br, s), 1.7 (2 H, br, s), 3.38 (2 H, br, s), 6.5-6.7 (2 H, br, s, aromatic); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 14.05, 22.67, 26.37, 29.22, 29.32, 29.40, 29.48, 29.62, 31.10, 31.89, 40.19, 108.33, 111.50, 118.30, 123.48, 163.46, 175.16; Anal. calcd for ($C_{20}H_{27}NO_2$)n: C, 76.67; H, 8.62; N, 4.47. Found: C, 75.68; H, 9.2; N, 4.4.

2.4.3. Preparation of polymers of 3-substituted pyrroles with squaric acid

2.4.3.1. Preparation of poly (3-octylpyrrole-co-squaric acid) (14a)

This polymer (58%) was synthesized by condensing 3-octylpyrrole (0.18 g, 1 mmol) and squaric acid (0.11 g, 1 mmol) under the same conditions as described for **11a**. IR ν_{max} (KBr) 3305, 2924, 2858, 1610, 1530, 1410, 1100, 890 cm^{-1}; UV λ_{max} (DMSO) 604 nm; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 0.9 (3 H, t, CH$_3$), 1.2 (12 H, m, CH$_2$), 4.75 (2 H, t, CH$_2$), 7.35 (1 H, m, aromatic), 10.55-10.95 (1 H, br, s, NH); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 14.01, 22.61, 27.26, 27.92, 29.23, 30.31, 31.83, 34.01, 74.26, 112.68, 128.08, 165.85, 180.64; Anal. calcd for $(C_{16}H1_9NO_2)_n$: C, 74.70; H, 7.39; N, 5.44. Found: C, 75.9; H, 7.69; N, 5.15.

2.4.3.2. Preparation of poly (3-dodecylpyrrole-co-squaric acid) (14b)

The title polymer (**14b**) (90 mg, 60%) was prepared from squaric acid (57 mg, 0.5 mmol) and 3-dodecylpyrrole (0.11 g, 0.5 mmol) according to the procedure used for the preparation of **11a**. IR ν_{max} (neat) 3336, 2931, 2859, 1765, 1730, 1615, 1550, 1514,1467,1159 cm^{-1}; UV λ_{max} (CHCl$_3$) 613 nm, (DMSO) 624 nm; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.9 (3 H, t, CH_2), 1.2 (20 H, m, CH_2), 2.6 (2 H, t, CH_2), 6.35 (1 H, br, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14,11, 15.21, 22.7, 29.41, 29.27, 30.46, 31.95, 47.46, 63.90, 102.0, 104.06, 128.11, 138.52, 159.14, 159.43, 161.88, 171.94; Anal. calcd for $(C_{20}H_{27}NO_{20})_n$ C, 76.67; H, 8.62; N, 4.47. Found: C, 76.20; H, 9.1; N, 4.3.

2.4.3.3. Preparation of poly (3-octylpyrrole-co-squaric acid) (15a)

Squaric acid (0.114 g, 1 mmol) and **8a** (0.18 g, 1 mmol) were stirred for 48 h in a mixture of acetic anhydride (7.5 mL) and 1-butanol (7.5 mL) under nitrogen atmosphere at room temperature. After work-up as described for the preparation of polymer **12**, the title polymer **15a** was obtained in a 58% yield. IR ν_{max} (KBr) 3361, 2930, 2859, 1755, 1688, 1623, 1545, 1402, 1115 cm^{-1}; UV λ_{max} (DMSO) 596 nm; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.9 (3 H, t, CH_3), 1.2 (12 H, m, CH_2) 4.75 (2 H, t, CH_2), 7.35 (1 H, m, aromatic), 10.55-10.95 (1 H, br, s, NH); ^{13}C NMR spectrum ($CDCl_3$, 22.5 MHz) δ 14.01, 22.61, 27.26, 27.92, 29.23, 30.31,31.83, 34.01, 74.26, 112.68, 128.08, 165.85, 180.64; Anal. calcd for $(C_{16}H_{19}NO_2)_n$: C, 74.70; H, 7.39; N, 5.44. Found: C, 75.9; H, 7.69; N, 5.15.

2.4.3.4. Preparation of poly (3-dodecylpyrrole-co-squaric acid) (15b)

This compound (90 mg, 58%) was prepared from squaric acid (57 mg, 0.5 mmol) and 3-dodecylpyrrole (0.11 g, 0.5 mmol) under the same conditions as described for **15a**. IR ν_{max} (KBr) 3345, 2963, 2859, 1724, 1662, 1537, 1473, 1112, 876 cm^{-1}; UV λ_{max} ($CHCl_3$) 612 nm, (DMSO) 623 nm; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 0.9 (3 H, t, CH_2), 1.2 (20 H, m, CH_2), 2.6 (2 H, t, CH_2), 6.35 (1 H, br, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.11, 15.21, 22.7, 29.41, 29.77, 30.46, 31.95, 47.46, 63.90, 102.0, 104.06, 128.11, 138.52, 159.14, 159.43, 161.88, 171.94;

Anal. calcd for $(C_{20}H_{27}NO_2)_n$: C, 76.67; H, 8.62; N, 4.47. Found: C, 76.20; H, 9.1; N, 4.3.

2.4.3.5. Preparation of poly (3-octylpyrrole-co-squaric acid) (16a)

Squaric acid (0.114 g, 1 mmol) and **8a** (0.18 g, 1 mmol) were stirred for 48 h in a mixture of glacial acetic acid (7.5 mL) and DMSO (7.5 mL) under nitrogen atmosphere at room temperature. The work-up procedure for the polymer **16a** was the same as used for the polymer **13**. The title polymer **16a** was obtained in a 58% yield after drying in a vacuum oven at 40 °C for 48 h. IR ν_{max} (KBr) 3361, 2930, 2859, 1755, 1688, 1623, 1545, 1402, 1115 cm^{-1}; UV λ_{max} (DMSO) 596 nm; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.9 (3 H, t, CH_3), 1.2 (12 H, m, CH_2) 4.75 (2 H, t, CH_2), 7.35 (1 H, m, aromatic), 10.55-10.95 (1 H, br, s, NH); ^{13}C NMR spectrum ($CDCl_3$, 22.5 MHz) δ 14.01, 22.61, 27.26, 27.92, 29.23, 30.31,31.83, 34.01, 74.26, 112.68, 128.08, 165.85, 180.64; Anal. calcd for $(C_{16}H_{19}NO_2)_n$: C, 74.70; H, 7.39; N, 5.44. Found: C, 75.9; H, 7.69; N, 5.15.

2.4.3.6. Preparation of poly (3-dodecylpyrrole-co-squaric acid (16b)

This compound (90 mg, 58%) was prepared from squaric acid (57 mg, 0.5 mmol) and 3-dodecylpyrrole (0.11 g, 0.5 mmol) under the same conditions as described for **16a**. IR ν_{max} (KBr) 3345, 2963, 2859, 1724, 1662, 1537, 1473, 1112, 876 cm^{-1}; UV λ_{max} ($CHCl_3$) 612 nm, (DMSO) 623 nm; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.9 (3 H, t, CH_2), 1.2 (20 H, m, CH_2), 2.6 (2 H, t, CH_2), 6.35 (1 H, br, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.11, 15.21, 22.7, 29.41, 29.77, 30.46, 31.95, 47.46, 63.90, 102.0, 104.06, 128.11, 138.52, 159.14, 159.43, 161.88, 171.94; Anal. calcd for $(C_{20}H_{27}NO_2)_n$: C, 76.67; H, 8.62; N, 4.47. Found: C, 76.20; H, 9.1; N, 4.3.

2.4.4. Preparation of model squaraine dyes

2.4.4.1. Preparation bis (1-dodecyl-2,4-dimethylpyrrolyl)squaraine (19)

This compound (72%) was prepared from **10** and **2** as per the same conditions as described for **20**. IR ν_{max} (neat) 2934, 2861, 1624, 1563, 1512, 1118 cm^{-1}; UV λ_{max} ($CHCl_3$) 580 nm, (DMSO) 583 nm. ^1H NMR ($CDCl_3$, 90 MHz) δ 0.85 (6 H, t, CH_3), 1.2 (40 H, m, CH_2), 2.25 (6 H, s, CH_3), 2.65 (6 H, s, CH_3), 4.65 (4 H, m, NCH_2), 6.05 (2 H, br, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 10.41, 13.12, 13.48, 14.11, 22.7, 24.34, 25.95, 26.73, 28.76, 29.05, 29.68, 31.35, 124.11, 138.94, 142.31, 168.18, 181.45.

2.4.4.2. Preparation of bis (2,4-dimethylpyrrolyl)squaraine (20)

This compound was prepared by using a reported procedure from 0.75 g (7.9 mmol) of 2,4-dimethylpyrrole (**9**) and 0.45 g (3.95 mmol) of squaric acid in acetic acid to give 0.74 g (71%) of **20**, mp, 240-250 °C (decomp). IR ν_{max} (KBr) 3230, 1635, 1610 cm^{-1}; UV λ_{max} ($CHCl_3$) 550 nm, (DMSO) 564 nm; ^1H NMR ($CDCl_3$, () MHz) δ 2.38 (6 H, s), 2.6 (6 H, s), 6.1 (2 H, s), 9.9-10.2 (1 H, br, D_2O exchangeable, NH); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 13.20, 14.2, 116.55, 125.30, 144.46, 169.90, 177.59; Anal. calcd for $C_{16}H_{16}N_2O_2$: C, 71.62 H, 6.01 N, 10.44. Found: C, 71.40 H, 6.11 N, 10.28.

2.5. References

1. *Handbook of Conducting Polymers*; Skotheim, T. J.; Ed.: Dekker. New York, **1986.**
2. Roncali, J. *Chem. Rev.* **1992**, *92*, 711.
3. Bredas, J. L., Chance, R. R., Eds. *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronic and Molecular Electronics*; Kluwer Academic publishers: Dordrecht, The Netherlands, **1990**.
4. Aldissi, M., Ed. *Intrinsically Conducting Polymers: An Emerging Technology*; Kluwer Academic Publishers: Dordrecht, The Netherlands, **1993**.
5. Bredas, J. L. *Synth. Met.* **1987**, *17*, 115.
6. Pranata, J.; Marudarajan, V. S.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2026.
7. Lee, Y.-S.; Kertesz, M.; Elsenbaumer, R. L. *Chem. Mater.* **1990**, *2*, 526.
8. Yu, L.; Dalton, L. R. *Macromolecules* **1990**, *23*, 3439.
9. Yu, L.; Chen, M.; Dalton, L. R. *Chem. Mater.* **1992**, *4*, 378.
10. Schluter, A.-D. *Adv. Mater.* **1991**, *3*, 282.
11. Kurti, J.; Surjan, P. R.; Kertesz, M. *J. Am. Chem. Soc.* **1991**, *113*, 9865.
12. Hanack, M.; Schmid, U.; Echinger, S.; Teichert, F.; Hieber, J. *Synthesis* **1993**, 634.
13. Tanaka, S.; Yamashita, Y. *Synth. Met.* **1993**, *55-57*, 1251.
14. Ferraris, J. P.; Bravo, A.; Kim, W.; Hrncir, D. C. *J. Chem. Soc., Chem. Commun.* **1994**, 991.
15. Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 1585.

16. Karikomi, M.; Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6791.
17. Treibs, A., Fritz, G. *Justus Liebigs Ann. Chem.* **1958**, *611*, 162.
18. Sprenger, H. E.; Ziegenbein, W. *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 894.
19. Sprenger, H. E.; Ziegenbein, W. *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 553.
20. Sprenger, H. E.; Ziegenbein, W. *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 530.
21. Schmidt, A. H. *Synthesis* **1980**, 961.
22. Law, K.-Y.; Bailey, F. C. *J. Imaging Sci.* **1987**, *31*, 172.
23. Law, K.-Y. *Chem. Rev.* **1993**, *93*, 449.
24. Morel, D. L.; Stogryn, E. L.; Piechowski, A. P. *J. Phys. Chem.* **1984**, *88*, 923.
25. Piechowski, A. P.; Bird, G. R.; Morel, D. L.; Stogryn, E. L. *J. Phys. Chem.* **1984**, *88*, 934.
26. Emmelius, M.; Pawlowski, G.; Vollmann, H. W. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1445.
27. Treibs, A.; Jacob, K. *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 694.
28. Treibs, A.; Jacob, K. *Justus Leibigs Ann. Chem.* **1966**, *699*, 153.
29. Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Polym. Bull.* **1992**, *29*, 119.
30. Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Synth. Met.* **1993**, *55-57*, 299.
31. Brocks, G. *J. Chem. Phys.* **1995**, *102*, 2522.
32. Brocks, G.; Tol, A. *J. Phys. Chem.* **1996**, *100*, 1838.
33. Ajayaghosh, A.; Chenthamarakshan, C. R.; Das, S.; George, M. V. *Chem. Mater.* **1997**, *9*, 644.
34. Wang, N.; Teo, K.; Anderson, H. J. *Can. J. Chem.* **1977**, *55*, 4112.
35. Guida, W. C.; Mathre, D. J. *J. Org. Chem.* **1980**, *45*, 3172.
36. Kakushima, M.; Hamel, P.; Frenette, R.; Rokach, J. *J. Org. Chem.* **1983**, *48*, 3214.

37. Greenhouse, R.; Ramirez, C.; Muchowski, J. M. *J. Org. Chem.* **1985**, *50*, 2961.

38. Yamamoto, T. *Chem. Lett.* **1996**, 703.

39. Griffiths, *J. Colour and Constitution of Organic Molecules*; Academic Press: Lonon, 1976.

40. Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.

41. Chen, C.-T.; Marder, S. R.; Chang, L.-T. *J. Am. Chem. Soc.* **1994.**, *116*, 3117.

42. Dirk, C. W.; Herndon, W. C.; Cervates-Lee, F.; Selnau, H.; Martinez, S.; Kalamegham, P.; Tan, A.; Campos, G.; Velez, M.; Zyss, J.; Ledoux, I.; Cheng, L.-T. *J. Am. Chem. Soc.* **1995**, *117*, 2214.

43. DeBolt, S. E.; Kollman, P. A. *J. Am. Chem. Soc.* **1990**, *112*, 7515.

44. Karelson, M.; Zerner, M. C. *J. Am. Chem. Soc.* **1990**, *112*, 9406.

45. Lerf, C.; Suppan, P. *J. Chem.Soc. Faraday Trans.* **1992**, *88*, 963.

46. Kamlet, M. J.; Abboud, J.- L.; Abraham, M. A.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.

47. Garnier, F.; Yassar, A.; Hajlaui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716.

48. McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910.

49. Winokur, M. J.; Prosa, T.J.; Moulton, J.; Smith, P.; Heeger, A. J. *Macromolecules* **1992**, *25*, 4364.

50. Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.

CHAPTER 3

PYRROLE-DERIVED WATER SOLUBLE OLIGOSQUARAINES: SYNTHESIS AND PROPERTIES OF SQUARAINE DYE BASED SELF-DOPED CONDUCTING MATERIALS

3.1. Introduction

Conjugated polymers, in general, can be transformed into electrically conducting materials by doping with appropriate dopants. Traditionally, doping can be achieved either by chemical or electrochemical methods. This kind of external doping produces highly charged polymer backbones either by oxidation or reduction processes. The doping process is often reversible and the counterions are free to migrate in and out of the polymer chains. In addition, externally doped conjugated polymers are highly insoluble and intractable. These drawbacks of conjugated polymers make them difficult to process thereby restricting their practical applications.

The concept of self-acid-doped conducting polymer was introduced by Patil *et al.* by covalently attaching an organic dopant to a π-conjugated polymer backbone.[1,2] After this discovery, synthesis and properties of several self-acid-doped conducting polymers have been reported in the literature. They include self-acid-doped polythiophenes,[3-8] polypyrroles[9-11] and polyanilines,[12-17] in which, the self-doping is achieved by covalently attaching alkylsulfonic acid or phosphonic acid groups on to the polymer backbone (Chart 1). In addition to providing water solubility, the sulfonate or phosphonate groups serve as charge balancing counter ions when the polymers are oxidatively doped.

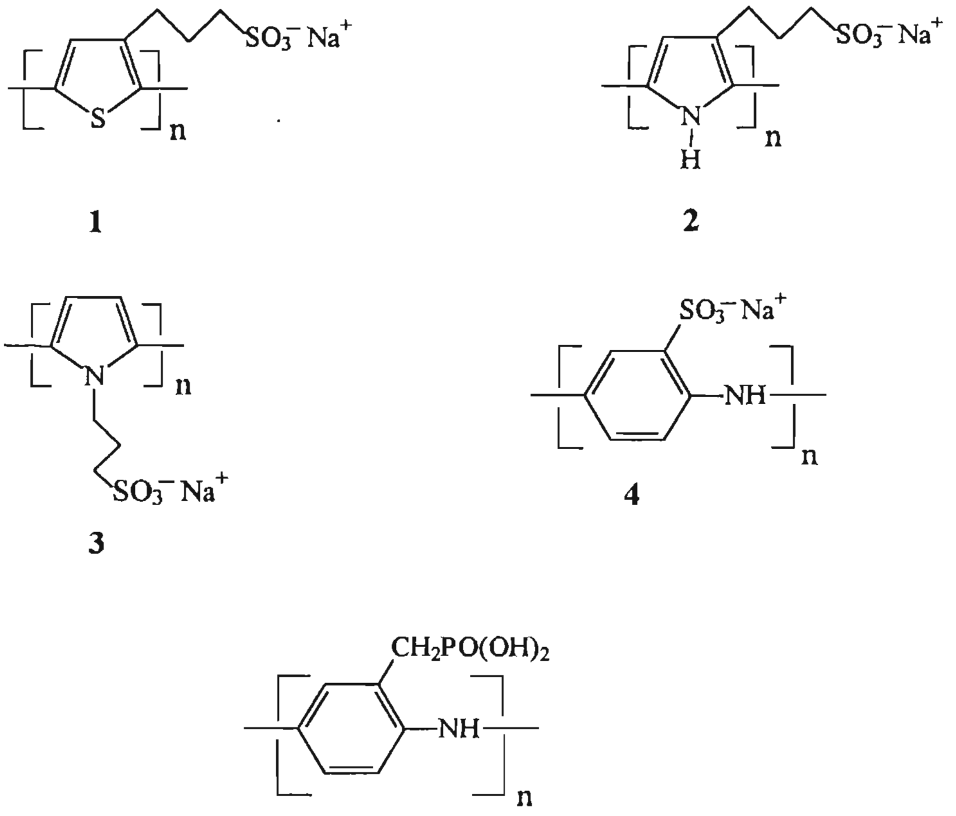


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Chart 1

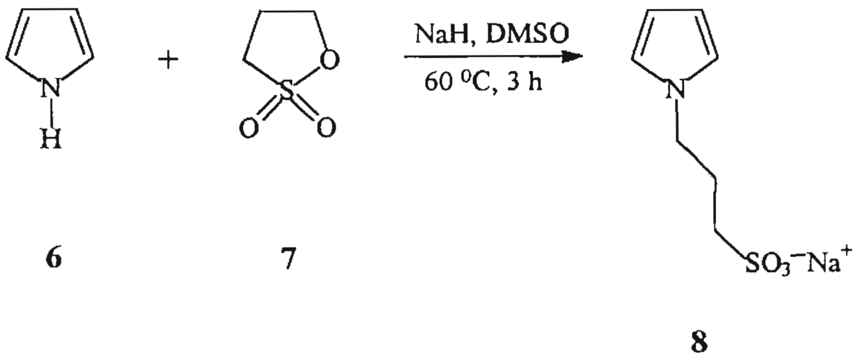
Most of the known self-acid-doped conducting polymers are based on the conventional polythiophenes, polypyrroles or polyanilines the synthesis of which are usually accomplished either by chemical or electrochemical polymerization of the corresponding monomers, attached to an appropriate organic dopant molecule. The use of "foreign" conducting salts as oxidants during the synthesis involves the chances of external doping of the resultant polymers, with doubtful identity of self-doping in many cases. The best way to solve this problem is to avoid the use of catalysts which may also act as "foreign" dopants during polymerization. A polycondensation route to self-acid-doped polymers, therefore, is a desirable synthetic alternative to such nondiscriminating oxidative polymerization strategies. Moreover, this approach would provide opportunity to combine the characteristic properties of the individual monomers, to form polymers with modified properties. Even though the polycondensation approach has been employed for the synthesis of several π-conjugated conducting polymers,[18-21] there are no reports on the use of such an approach to the synthesis of self-doped conducting polymers. It is known in the literature that the reaction of pyrrole with squaric acid results in the formation of insoluble and infusible materials.[22, 23]

We have already shown in Chapter 2 that soluble low bandgap polymers can be prepared by the polycondensation reaction of squaric acid with appropriate pyrrole derivatives. Such polymers showed intrinsic conductivities to a certain extent and their conductivities could be further enhanced on doping with appropriate dopants. In this context, doping with organic sulfonic acid derivatives has significance because covalent attachment of such dopant molecules to macromolecular squaraines may result in water soluble self-acid-doped conducting materials. In the present Chapter, synthesis and properties of several water soluble oligomeric squaraines, containing covalently attached alkylsulfonate acid groups are described.

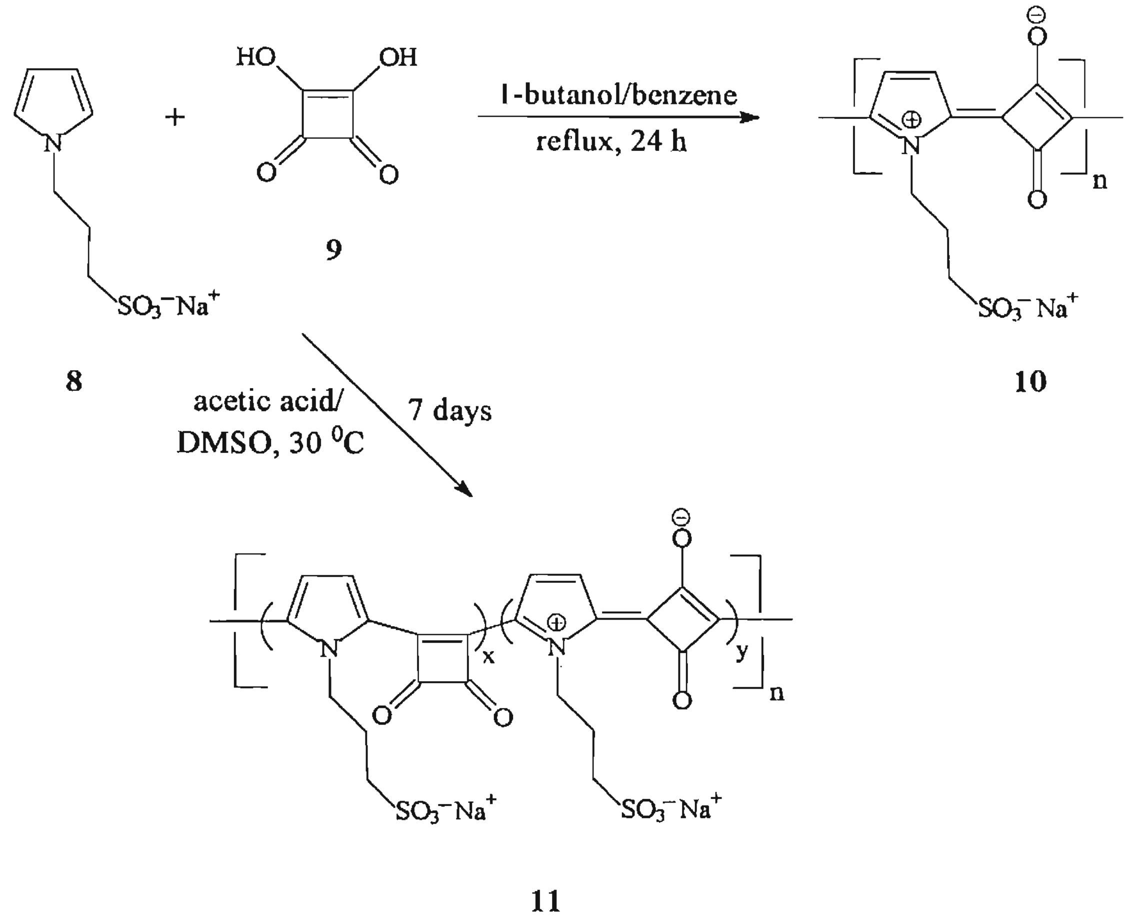
3.2. Results and Discussion

3.2.1. Synthesis of the oligomers 10 and 11

The starting material, sodium 3-(pyrrol-1-yl)propane sulfonate **8** for the preparation of the oligomers **10** and **11**, was synthesized as per Scheme 1. The reactions of pyrrole (**6**) with 1,3-propane sultone (7) in the presence of sodium hydride gave the pyrrole derivative **8** in a 76% yield. The product **8** was characterized by spectral and elemental analyses. The oligomers **10** and **11** were prepared by the condensation of squaric acid with **8** in 1-butanol/benzene solvent mixture under reflux conditions or by using acetic acid/DMSO mixture at room temperature as shown in Scheme 2. The reaction mixture in each case was poured into chloroform and the product obtained was repeatedly washed with 1-butanol to get the oligomers **10** and **11** in 86 and 58% yields respectively. These materials were soluble in water, DMF and DMSO. The molecular weights of **10** and **11** were determined by gel permeation chromatography after hydrolysing to the corresponding sulfonic acids. The hydrolysis of **10** and **11** was necessary to improve their solubility in THF which is used as the eluting solvent. Determination of the molecular weights revealed that **10** and **11** have very low degree of polymerization restricting them to the oligomeric stage (Mn ~ 2800-3000). This could be due to the premature precipitation of the products from the reaction mixture, thereby terminating the polycondensation.



Scheme 1

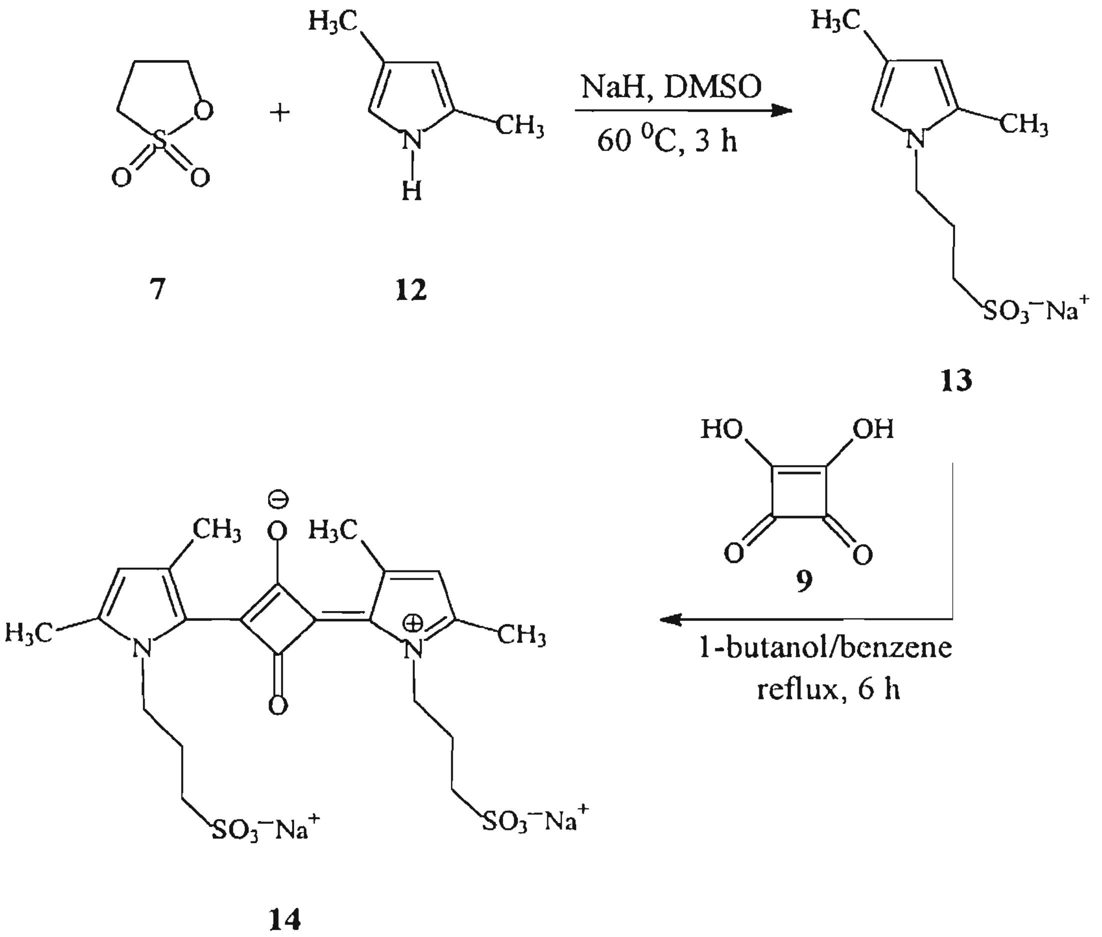


Scheme 2

The IR spectrum of **10** showed the characteristic absorption peak at 1629 cm^{-1} of the cyclobutenediylium-1,3-diolate, which is a general feature of the zwitterionic squaraine dyes. In the case of the oligomer **11**, in addition to the absorption peak at 1629 cm^{-1}, two strong carbonyl absorptions at 1740 and 1770 cm^{-1} were also observed which correspond to a 1,2-disubstituted cyclobutene-3,4-dione moiety. This observation was in accordance with our earlier finding that the condensation of pyrrole derivatives with squaric acid in 1-butanol/benzene mixture gave polymers containing mainly 1,3-oriented zwitterionic repeat units, whereas polymers prepared in acetic acid/DMSO mixture consist of both zwitterionic and diketonic repeat units. The other characteristic absorption peaks of **10** and **11** are 2941 (saturated C-H stretching), 1198 (asymmetric $S(=O)_2$ stretching), and 1053 cm^{-1} (symmetric $S(=O)_2$ stretching) which support the presence of the propane sulfonate group in both the oligomers. The strong and broad OH stretching absorption peak at 3444 cm^{-1} indicated the presence of adsorbed water molecules, which are difficult to remove even after prolonged drying in a vacuum oven.

The ^1H NMR spectra of **10** and **11** in DMSO-d_6 showed absorption signals at δ 6.0 and 6.85 characteristic of the two pyrrole protons which are observed as broad signals. In this case, it is worth mentioning that in the case of several pyrrole-derived self-acid-doped conducting polymers, the aromatic protons of the pyrrole ring appeared as broad signals and in some cases it was even difficult to observe those signals.[11] In oligomers **10** and **11**, the aliphatic protons attached to the pyrrole nitrogen appeared as a broad triplet around δ 4.65 which is 0.88 ppm deshielded from that of the starting pyrrole **8**. The protons attached to the sulfonate group appeared as a broad triplet around δ 2.2, whereas, the middle CH_2 protons of the propane side chain appeared as a broad multiplet around δ 1.6.

Much information on the structure and property of the oligomers **10** and **11** could be obtained from studies of their model compounds. In this context, we have synthesized a water soluble model squaraine dye **14** for a comparison of its structure and properties with those of the oligomers **10** and **11**. The starting compound **13** of the model dye **14** was prepared from commercially available 2,4-dimethylpyrrole (**12**) by the reaction of propane sultone (**7**) as per Scheme 3.



Scheme 3

The product **13** was obtained in 88% yield and was characterized on the basis of spectral data and elemental analysis. The model compound **14** was prepared through the condensation of **13** with squaric acid in 1-butanol-benzene mixture (Scheme 3). The IR spectra of the model compound **14**, and the oligomers **10** and **11** are shown in Figure 1. The characteristic absorptions of **10** and **14** are in close proximity to each other. For example, the IR spectrum of **14** shows a strong peak around 1620 cm^{-1}, which is characteristic of the cyclobutenediylium-1,3-diolate of the squaraine unit as in the case of the oligomer **10**. In addition, the absorption peaks at 2933 (aliphatic CH_2 stretching), 1189 (asymmetric $S(=O)_2$ stretching) and 1048 cm^{-1} (symmetric $S(=O)_2$ stretching) closely resemble to those of the oligomer **10**.

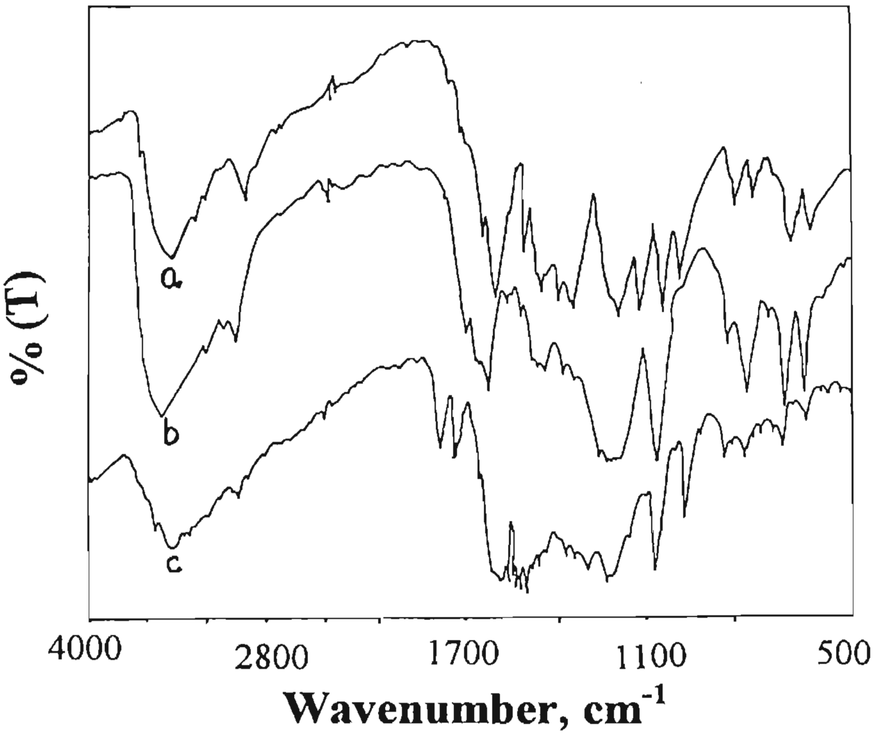


Figure 1. IR spectra of (a) model compound **14** and oligomers (b) **10**, (c) **11**

The ^1H NMR spectrum of the model compound **14** is shown in Figure 2. The aromatic protons of the two pyrrole rings appeared as a singlet around δ 6.25. The side chain protons attached to the pyrrole nitrogen appeared as a triplet at δ 4.75. The peaks at δ 1.7-1.95 equivalent to four protons were assigned for the two CH_2 groups attached to the sulfonate moiety. The four CH_3 groups attached to the two pyrrole rings gave two singlets around δ 1.9 and 2.1. The ^{13}C NMR spectrum

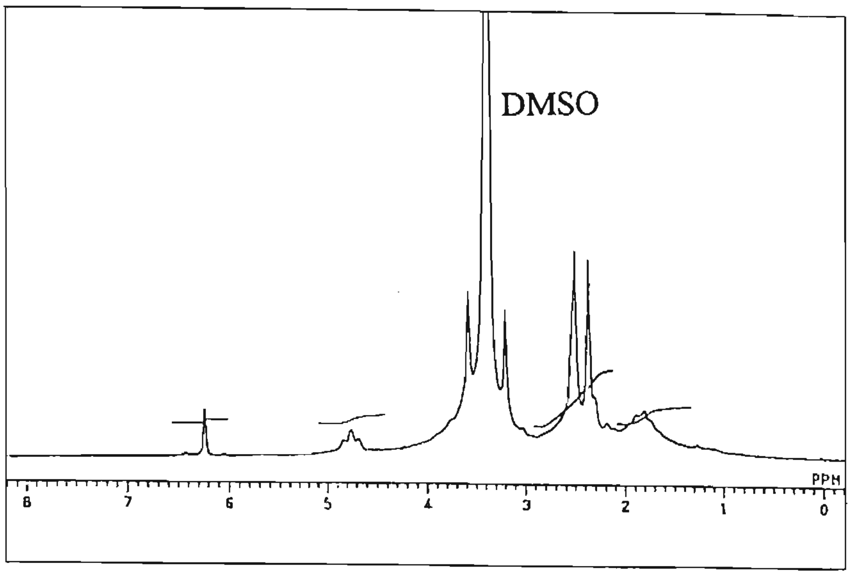


Figure 2. ^{1}H NMR spectrum of the model compound **14**

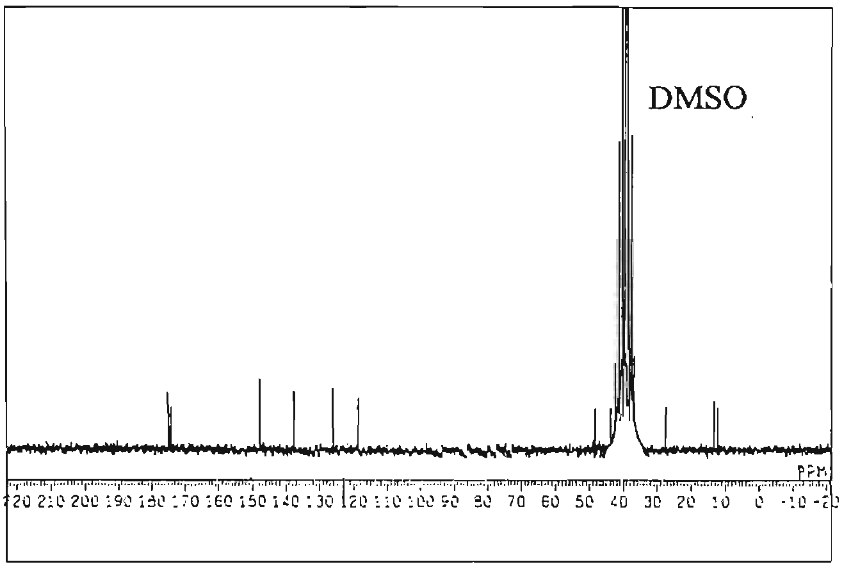


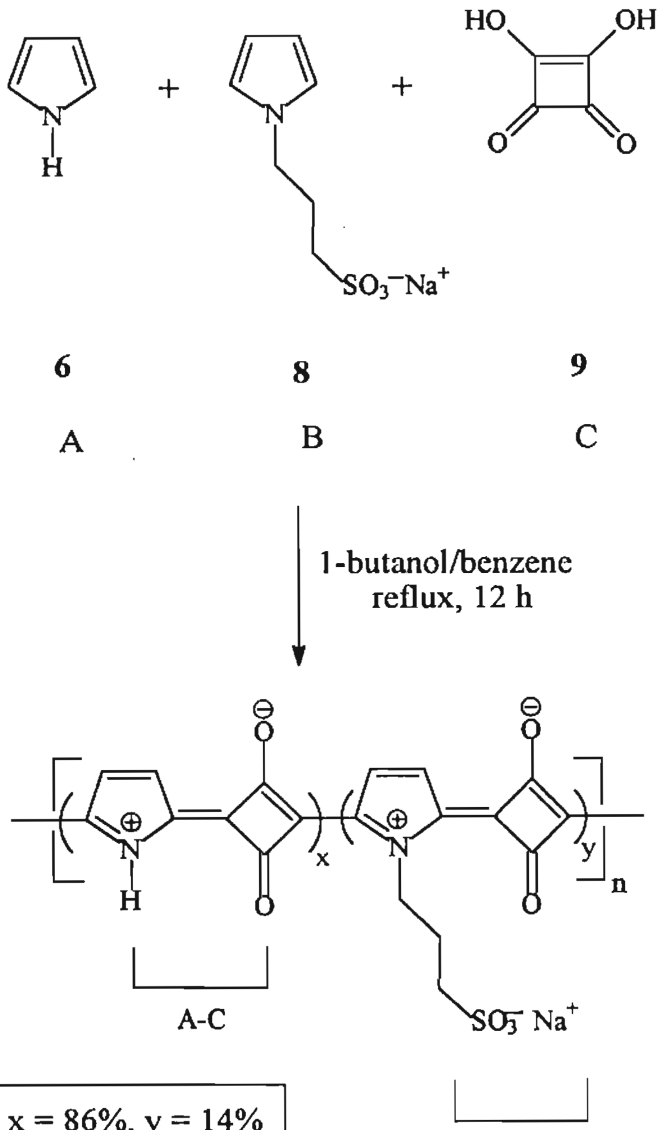
Figure 3. ^{13}C NMR spectrum of the model compound **14**

of **14** showed five quaternary carbon signals, one tertiary carbon signal, three secondary carbon signals and two primary carbon signals (Figure 3). The quaternary carbon signals at 174.21 and 175 ppm were assigned for the four carbon atoms of the cyclobutene ring. The signals at 119.07, 126.23, 137.48, and 147.77 ppm were attributed to the pyrrole carbon atoms, whereas, the signals at 27.45, 43.14, and 48.12 ppm could be assigned to the six carbon atoms of the two propane side chains. The carbon atoms of the four methyl groups attached to the two pyrrole rings appeared at 14.71 and 15.66 ppm. The observed NMR and IR spectral features reveal that the compound **14** has a resonance stabilized zwitterionic structure in which the two halves of the molecule are identical. The elemental analysis data of **14** was in agreement with its structure. The structures of the oligomers **10** and **11** were assigned on the basis of comparison of their spectral features with those of the model dye **14**.

3.2.2. Synthesis and characterization of the random oligomers 15a-d

The random oligomers **15a-d** of squaric acid (**9**) with pyrrole (**6**) and sodium 3-(pyrrol-1-yl)propane sulfonate (**8**) were synthesized as per Scheme 4. This reaction can be considered as the condensation polymerization between three different monomers A, B and C leading to the formation of (A-C)-(B-C) type copolymers having random distribution of the repeat units A-C and B-C, as shown in the general Scheme 5. Here, the monomer C is reactive towards both A and B, whereas A and B are nonreactive to each other. Hence, only two types of repeat units, A-C and B-C, can be formed as shown in Scheme 5.

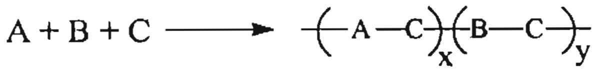
Several random oligomers of squaric acid with various compositions of the pyrroles **6** and **8** were prepared by polycondensation reaction using a 2:1 mixture of 1-butanol-benzene as solvent under reflux conditions, as shown in Scheme 4. The bluish green products that precipitated were collected by filtration and washed



15a-d

15a, x = 86%, y = 14%
15b, x = 70%, y = 30%
15c, x = 54%, y = 46%
15d, x = 28%, y = 72%

Scheme 4



$$A + B + C \longrightarrow \left(A - C \right)_x \left(B - C \right)_y$$

Scheme 5

thoroughly with 1-butanol and chloroform. The molecular weights of the condensation products **15a-d**, determined by gel permeation chromatography gave number average molecular weights in the range of 3000-4000 atomic mass units. The IR spectra of **15a-d** having various monomer compositions showed similarities to the spectral features of the oligomer **10**. The IR spectral values of **10**, **14** and **15d** are given in Table 1 for comparison.

Table 1. IR spectral data (cm^{-1}) of the oligomer **10**, random oligomer **15d** and the model dye **14**.

Oligomer/ Model dye	O-H and/or N-H stretching	Aliphatic C-H stretching	C-O stretching	$S(=O)_2$ asymmetric stretching	$S(=O)_2$ symmetric stretching
14	3423	2933	1620	1189	1048
10	3444	2941	1629	1198	1053
15d	3406	2940	1600	1223	1045

The ^1H NMR spectra of the random oligomers **15a-d** in DMSO showed broad peaks corresponding to the protons of the pyrrole moieties around δ 6.0 and 6.8. The other characteristic peaks were at δ 4.4 ($N\text{-}CH_2$), 2.3 ($-CH_2SO_3^-Na^+$) and 1.8

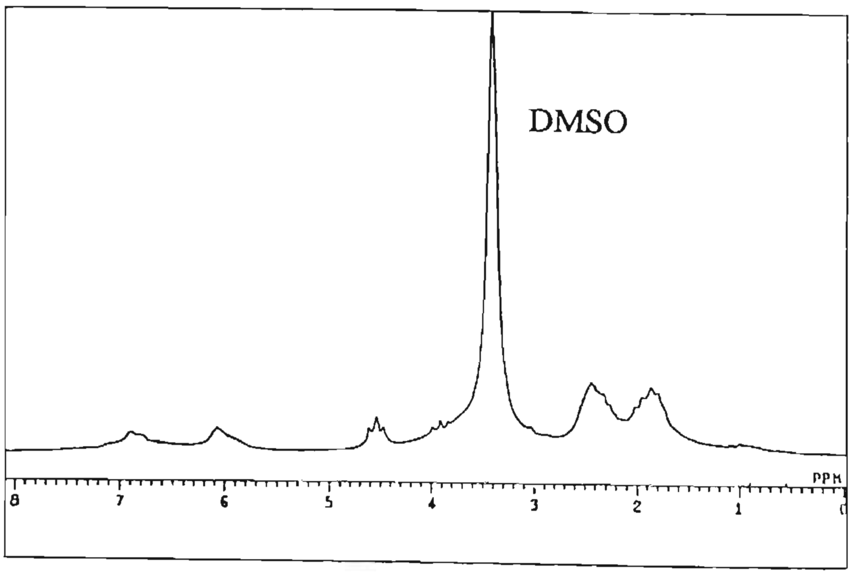


Figure 4. ^{1}H NMR spectrum of oligomer **10**

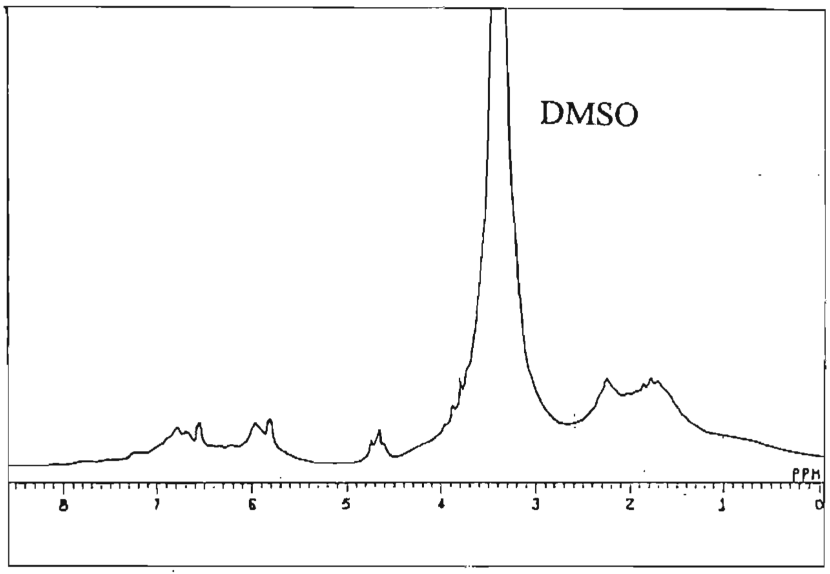


Figure 5. ^{1}H NMR spectrum of random oligomer **15d**.

(CH_2). The ^{1}H NMR spectra of the oligomer **10** and the random oligomer **15d** are shown in Figures 4 and 5 for comparison.

Since the random oligomer synthesis involves a 1:1 polycondensation, the total mole ratio of squaric acid and the two pyrrole monomers **6** and **8** were kept equal. Thus, random oligomers of various compositions were prepared by changing the mole ratio of the pyrrole monomers **6** and **8** in the feed composition in which their combined mole ratio with respect to squaric acid was 50%. The oligomer composition depends upon the reactivity of the two pyrrole monomers towards squaric acid. The oligomer compositions in all the cases were determined by the elemental analysis and the data are presented in Table 2. A plot of the expected and observed mole percentages of the B-C repeat units in the oligomers **15a-d** involving the monomer **8** is shown in Figure 6. From Figure 6 it is clear that

Table 2. Expected and observed compositions of the random oligomers **15a-d**.

Oligomer	Feed composition of the monomers **6**, **8** and **9**, (mol%)			Observed composition of **6**, **8** and **9** in the oligomers, (mol%)*			Composition of repeat units in the oligomers	
	6	**8**	**9**	**6**	**8**	**9**	A-C	B-C
15a	40	10	50	43	7	50	86	14
15b	30	20	50	35	15	50	70	30
15c	20	30	50	27	23	50	54	46
15d	10	40	50	14	36	50	28	72

*determined by elemental analysis

the mole percentage of the B-C repeat units containing the monomer **8** is always less than the expected value, which reveals that the pyrrole **6** is more reactive towards squaric acid than the pyrrole derivative **8**. Hence, all the oligomers had higher content of the A-C repeat units of the monomer **6** with squaric acid than the B-C repeat units containing the monomer **8**.

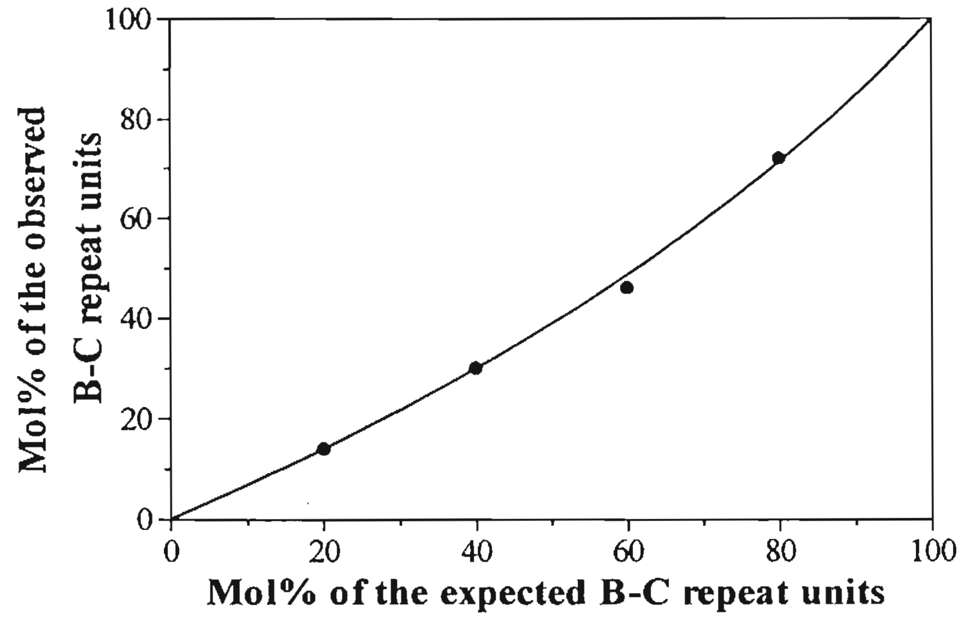


Figure 6. Relationship between the expected and observed compositions of the oligomers **15a-d.**

3.2.3. Absorption spectral studies of 10, 11, 14 and 15a-d

The UV-Vis absorption spectra of the oligomers **10**, **11** and **15a-d** and the model compound **14** were recorded in both water and DMSO. The absorption spectra of **10** and **14** in water and DMSO are compared in Figure 7. Considerable shift in the absorption bands could be noticed for both the compounds when the solvent was changed from water to DMSO. For example, the model compound **14** showed an intense sharp absorption maximum at 567 nm in water, which is red shifted to 584 nm in DMSO. However, in the case of the oligomer **10** the absorption was broad, both in DMSO and in water, indicating an extended conjugation compared to that of the model compound **14**. The oligomer **10** showed absorption maxima at 354, 574 and 612 nm in DMSO, whereas, in water the absorption maxima were at 354, 562 and 597 nm. The red shift for the absorption bands of the oligomer **10** in DMSO could be due to the solvent induced planarization of the π-conjugated oligomer backbone.

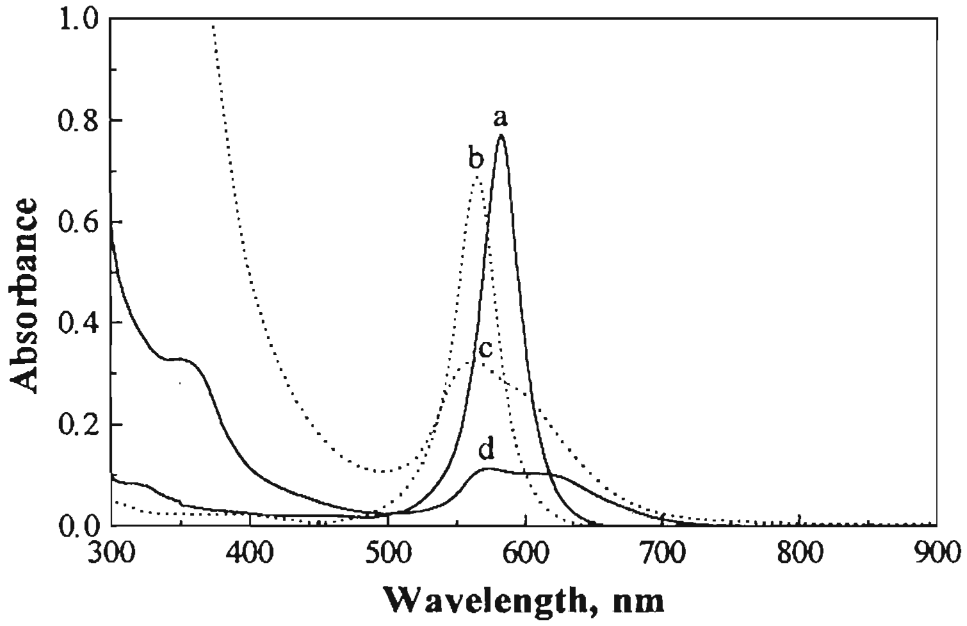


Figure 7. UV-Vis absorption spectra of model compound **14**, (a) in DMSO, (b) in water, and oligomer **10**, (c) in water, (d) in DMSO.

The UV-Vis spectra of the random oligomers **15a-d** were considerably different from those of the oligomers **10** and **11**. All random oligomers showed very broad absorption band, tailing to the near infra red (NIR) region. The optical absorption spectra of a representative random oligomer **15d**, recorded in DMSO and water are compared with those of the oligomers **10** and **11** in Figure 8. The long wavelength absorption of **15d** in DMSO showed an absorption maximum around 630 nm with two shoulders around 550 and 710 nm. The absorption spectra of **10** and **11** are relatively blue shifted compared to that of **15d**. This observation reveals that the incorporation of the A-C repeat units in the oligomer

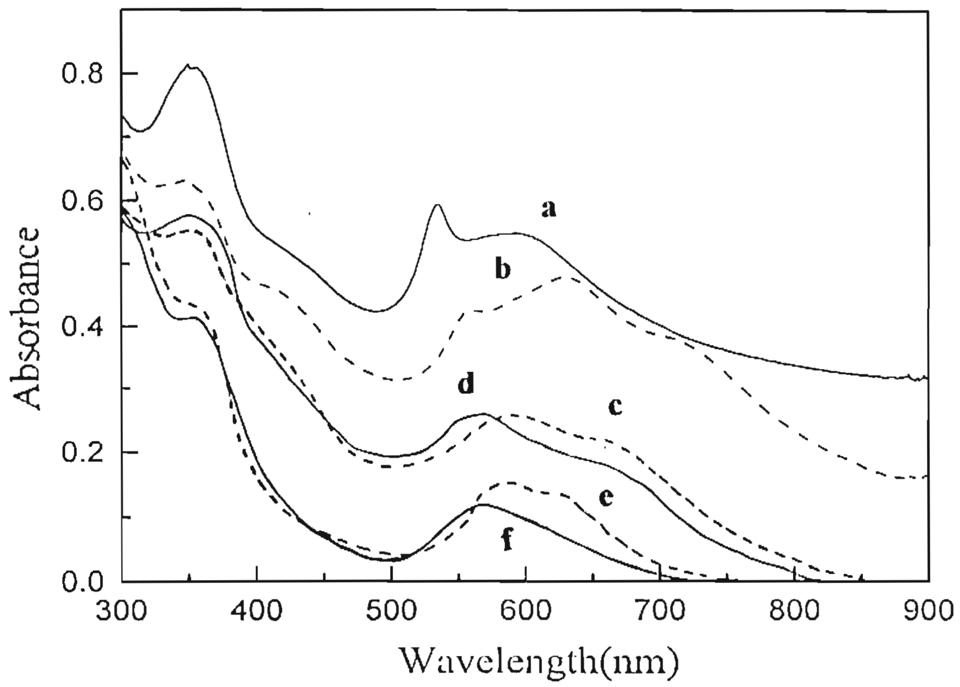


Figure 8. UV-Vis absorption spectra of **10**, **11** and **15d** in DMSO and water. (a) **15d** in water, (b) in DMSO; (c) **11** in DMSO, (d) in water; (e) **10** in DMSO, (f) in water.

10 has considerable influence in its absorption spectra, which could probably be due to the enhanced conjugation and planarization of the oligomeric structure. In water, all oligomers show considerable blue shift of the absorption maxima which can be attributed to the strong hydrogen bonding of water with the oligomeric repeat units.

3.2.4. Solvent effects on absorption spectra of 10, 14 and 15a-d

Solvatochromic properties of the oligomer **10**, the random oligomers **15a-d** and the model compound **14** were studied in water and alcoholic solvents. In hydrogen bonding (HBD) solvents such as MeOH, EtOH, 2-PrOH and 1-BuOH, a hypsochromic shift of the long wavelength absorption is noticed with increase in hydrogen bonding ability (acidity) of the solvents. This observation is in

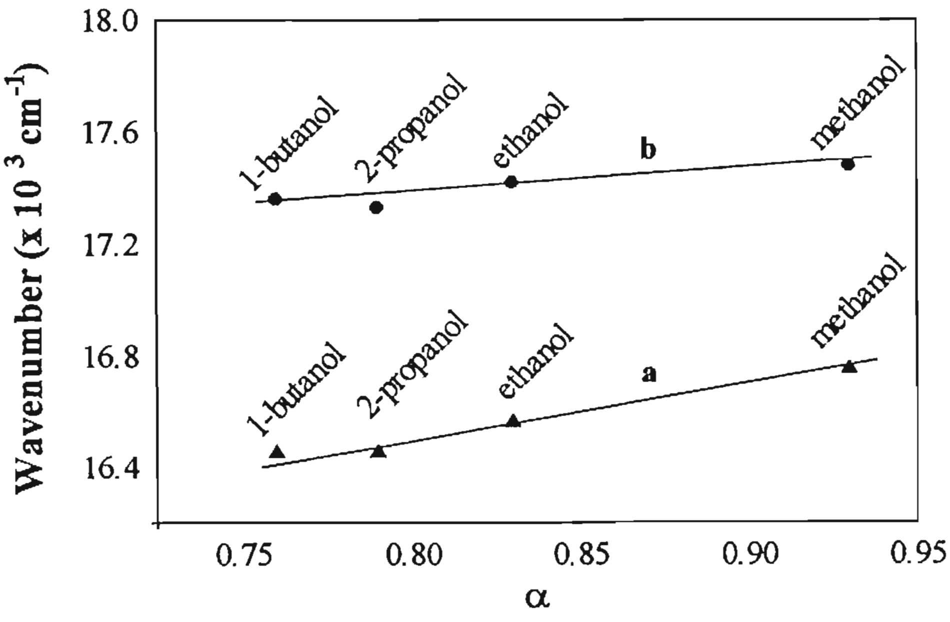


Figure 9. Plot of the absorption maxima of (a) oligomer **10** and (b) model dye **14** versus the solvent acidity parameter.

agreement with those of other squaraine dyes and polysquaraines having zwitterionic structures. Therefore, the observed solvent effect on the absorption spectra of the new oligomers and their model squaraine dye support their zwitterionic structures which are less polar in the excited state than in the ground state. In the ground state, oligosquaraines and their model dye form hydrogen bonds with protic solvents. The observed spectral shift depends upon the ability of the solvents to form specific hydrogen-bonded solute solvent complexes.[24,25] A linear dependence was noticed when the absorption maxima of the oligomers **10**, **15a-d** and the model dye **14** in various HBD solvents were plotted against their α–scale (acidity of the HBD solvent) which is the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond.[26,27] This has been exemplified in the case of the oligomer **10** and the model dye **14** as shown in Figure 9. Similar negative solvatochromic relationship in hydrogen bonding solvents are reported for several squaraine dyes.[28,29]

3.2.5. Thermogravimetric analysis of the oligomers 10, 11 and 15a-d

The thermograms obtained by the thermogravimetric analysis (TGA) of the oligomers **10, 11** and the random oligomers **15a-d** are shown in Figure 10. TGA was carried out at a heating rate of 20 °C/min under nitrogen atmosphere. The initial weight loss of nearly 5-10%, below 200 °C, reveals the presence of adsorbed water molecules in all the oligomers. The thermal decomposition of the oligomer chains occur between 350- 450 °C and in all the cases nearly 60% weight loss is noticed at this temperature. Comparison of the thermograms of the various random oligomers with different pyrrole compositions did not show any major difference in the general pattern of the thermal decomposition. The differential scanning colorimetry (DSC) analysis revealed no melting transition to any of the polymers probably due to their zwitterionic structure.

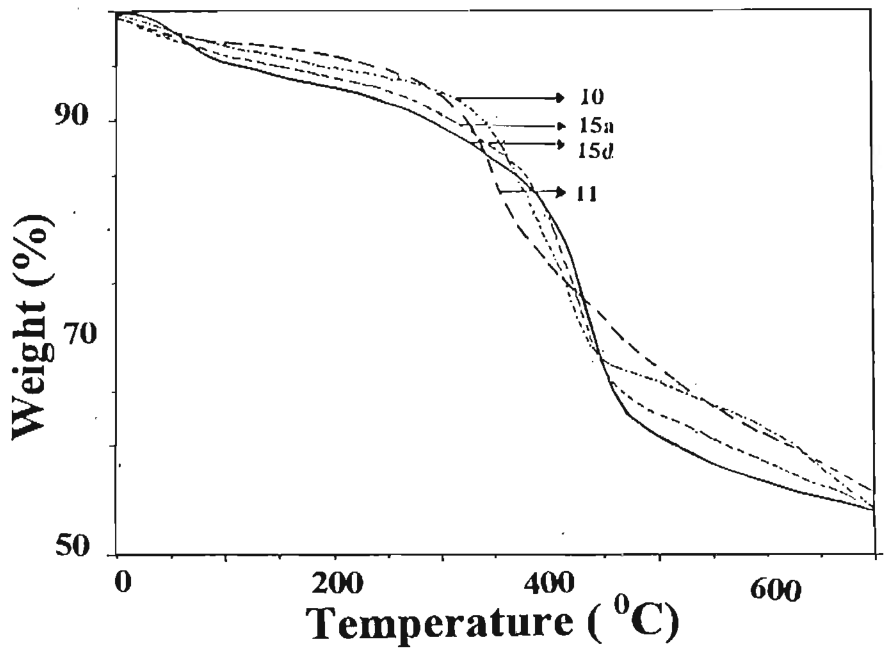


Figure 10. TGA of oligomers **10**, **11** and the random oligomers **15a**, **15d**.

3.2.6. X-ray diffraction studies

X-ray diffraction patterns of the oligomers **10** and **15d** are shown in Figure 11. All the oligomers showed a first order reflection at 2θ angle of ~5.0° which corresponds to an interlayer d-spacing of 18 Å. This is the characteristic of the well-organized lamellar assembly similar to those of polythiophenes and polypyrroles. However, this value is slightly higher compared to that of a similar polysquaraine having propyl side chain. Similarly, the corresponding values for the first order reflections in polythiophenes and polypyrroles are also smaller compared to those of **10** and **15d**. This could probably be due to the strong electrostatic repulsion of the ionic groups of the propyl side chains in oligomers **10** and **15d**. A broad and diffused scattering peak ranging from 2θ = 15-25° corresponding to the d-spacing of 4-3.5 Å could also be found for the oligomers **10** and **15d**. The broad diffraction at this wide angle area can be attributed to the disruption of the stacking of the polymer chains due to the presence of disordered phase.

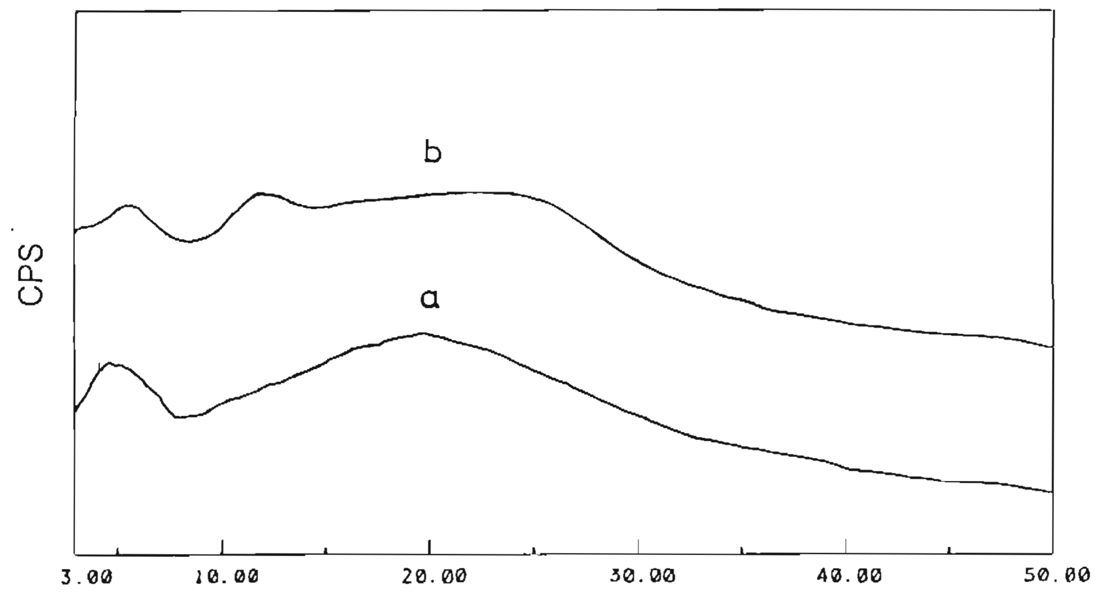
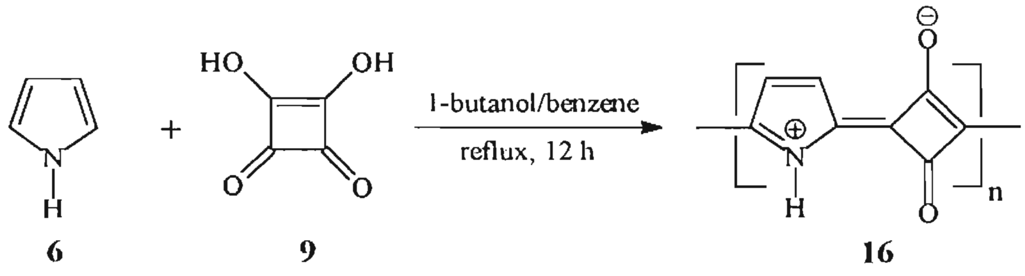


Figure 11. X-ray diffraction patterns of (a) oligomer **10** and (b) random oligomer **15d**.

3.2.7. Electrical conductivity of the oligomers 10, 11 and 15a-d

Electrical conductivity of the oligomers **10, 11** and **15a-d** were measured by the standard four probe method using pressed pellets at room temperature. These values are listed in Table 3. For the purpose of comparison, the condensation



Scheme 6

product **16** of pyrrole and squaric acid was prepared as per Scheme 6 and its conductivity was measured using the four-probe method under identical conditions. All the new oligomers showed enhanced conductivities in comparison to that of **16**. For example, the specific conductivity of **16** is found to be 1.1 x 10^{-6} S/cm whereas, in the case of the oligomer **10** in which the pyrrole NH is replaced

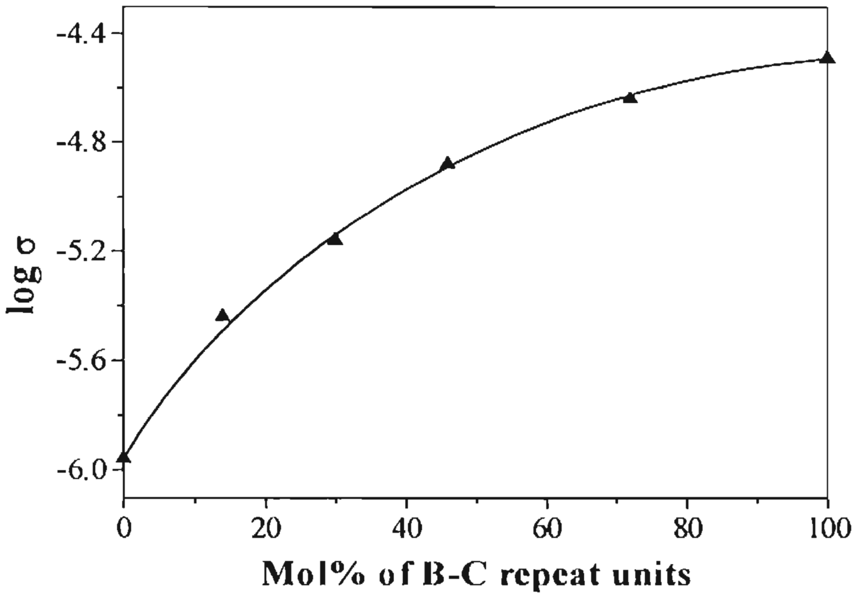


Figure 12. Plot of logarithmic conductivity versus copolymer composition.

by the N-propanesulfonic acid group showed enhanced conductivity of 3.2 x 10^{-5} S/cm. The specific conductivities of the oligomers **15a-d** depend upon their oligomeric compositions. A plot of the logarithmic conductivity of **15a-d** versus their oligomeric compositions is shown in Figure 12, which shows enhancement in the conductivities of **15a-d** with the increase in mole percentage of the B-C repeat units.

3.2.8. Effect of polymeric additives on conducting properties of the oligomers 10 and 15a-d

Blending of two or more polymers is a usual procedure to modify their physical properties for specific applications. Since conjugated conducting polymers without long flexible side chains are brittle, particularly after doping, blending with conventional polymers in order to improve their mechanical properties and processability has been studied in several cases. Therefore, several π-conjugated conducting polymers such as polythiophenes and polypyrroles have been subjected to blending studies with conventional polymers containing flexible side chains in order to improve their mechanical properties and processability at the expense of their conductivities.[30-34] In this context, we have examined the effect of polymeric additives such as poly(vinylpyrrolidone) (PVP) and poly(vinylalcohol) (PVA) on the conductivities of the newly synthesized squaraine oligomers.

It is already known that optical properties of squaraine dyes are influenced by polymeric additives. For example, polymers such as poly(vinylpyrrolidone) and poly(vinylalcohol) are found to enhance the fluorescence quantum yields of several squaraine dyes. This has been explained on the basis of the formation of strongly hydrogen bonded squaraine-polymer complex. Therefore, it is anticipated that these polymeric additives have better compatibility with the squaraine unit due to electrostatic and hydrogen bonding interactions. It is also expected that the processability of the new squaraine oligomers can be improved on blending with polymeric additives containing flexible side chains.

Polymeric blends of the oligomers **10** and **15a-d** with various compositions of either PVP or PVA were prepared by the slow evaporation of their methanolic or water solutions. Polymeric films of these blends having reasonably good optical

Table 3. Conductivity values of oligomers **10**, **11** , **15a-d** and **16**

Polymer	Mol% of A-C repeat units	Specific conductivity (S/cm)
16	0	1.1×10^{-6}
15a	14	3.6×10^{-6}
15b	30	6.9×10^{-6}
15c	46	1.3×10^{-5}
15d	72	2.3×10^{-5}
10	100	3.2×10^{-5}

Table 4. Effect of PVP on the conductivity of the oligomer **10**.

Wt.% of PVP	Specific conductivity, (S/cm)
0	3.2×10^{-5}
5	1.8×10^{-5}
10	1.2×10^{-5}
15	1.1×10^{-5}
25	1.0×10^{-5}

Table 5. Effect of PVP on the conductivity of the random oligomer **15d**.

Wt.% of PVP	Specific conductivity (S/cm)
0	2.3×10^{-5}
5	1.0×10^{-5}
10	5.2×10^{-6}
15	3.3×10^{-6}
25	1.7×10^{-6}

quality could be prepared by casting the blended solution from methanol, which was difficult to obtain in the case of unblended squaraine oligomers due to their strong aggregation. The IR spectra of the blended oligomers did not show any difference from those of the oligomers before blending. However, the UV-Vis spectra of the blended oligomers exhibited a blue shift similar to the positive solvatochromic shift of the squaraine oligomers and polymers in protic hydrogen bonding solvents. This observation indicates strong interaction between the polymeric additives and the squaraine oligomers, which could be explained on the basis of hydrogen bonding or electrostatic interaction.

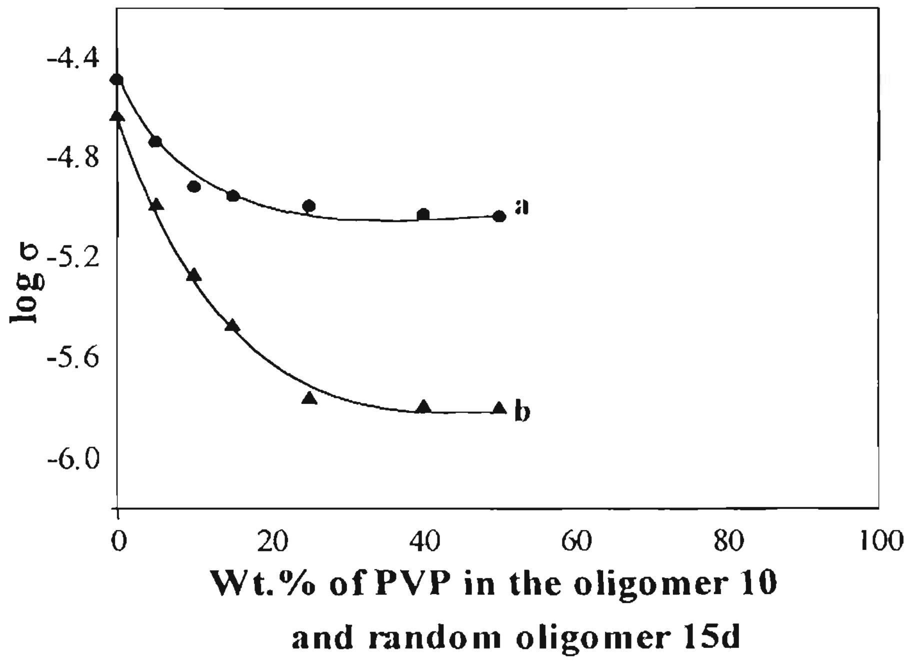


Figure 13. Effect of PVP on the conductivity of (a) oligomer **10** and (b) random oligomer **15d**.

The electrical conductivity of the blends having various compositions of PVP and the oligomer **10** are listed in Tables 4 and 5. It has been observed that the conductivity decreased with the increase in weight percentage of the polymeric additive in the blend. The effect of PVP on the conductivity of the oligomer **10** and the random oligomer **15d** are shown in Figure 13. As shown in this figure, the logarithmic conductivity decreased with the increase in weight percentage of the polymeric additive. The initial drop in conductivity was rapid with the addition of PVP or PVA to the oligomers. As the content of PVP or PVA increases further, the conductivity of the blends decreases slowly as shown in Figure 13. Similar

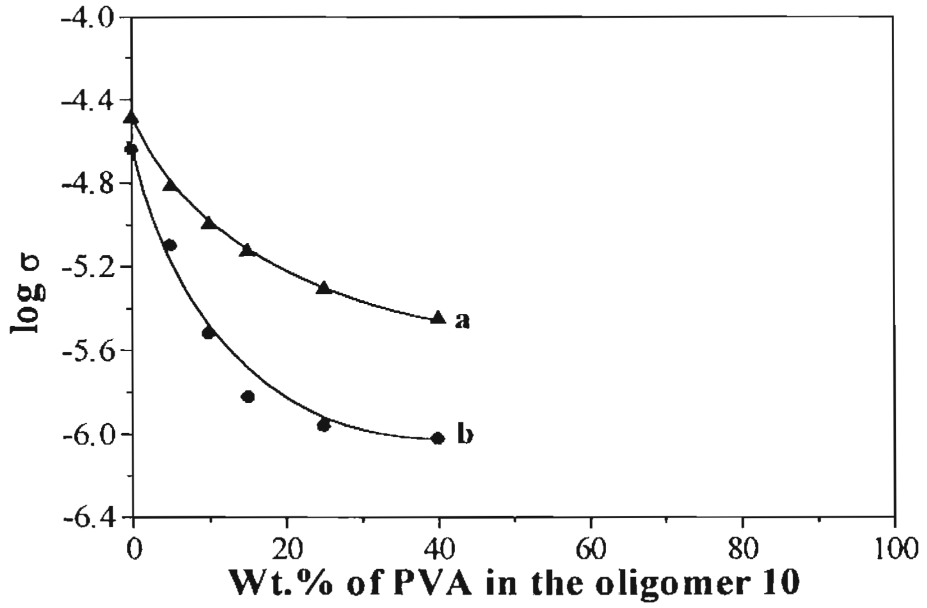


Figure 14. Effect of PVA on the conductivity of (a) oligomer **10** and (b) random oligomer **15d**.

effect was noticed in the case of blending PVA with the oligomer **10** and the random oligomer **15 d** as shown in Figure 14. Despite the decrease in conductivity, the processability of the polymers enhanced significantly on blending and thus free-standing optical quality films could be obtained.

3.3. Conclusions

Pyrrole, which is covalently attached to propane sulfonate moiety, on polycondensation with squaric acid gave a water soluble self-doped conducting oligomer. Significant improvements in water solubility and conductivity could be observed for this material compared to those of an analogous material **16** without the propane sulfonate groups. The structure and properties of this oligomer show resemblance to that of a model dye **14**. The properties of **10** could be manipulated by synthesizing the random oligomers **15a-d**. All the new squaraine oligomers showed enhanced conductivities compared to that of **16** without the propane sulfonate moiety. Optical quality films could be cast from these oligomers on blending with flexible polymers such as PVP and PVA, whereas their conductivity decreased with increase in weight percentage of the additive. The polycondensation approach towards self-doped conducting materials described in the present study could be a novel synthetic alternative to the nondiscriminating chemical or electrochemical oxidative polymerization strategies.

3.4. Experimental Section

The IR spectra were recorded on a Perkin Elmer model 882 Infrared spectrometer. The electronic absorption spectra were recorded either on a Shimadzu UV-2100 spectrophotometer, or on a GBC double beam UV-visible spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX 90 Spectrometer using tetramethylsilane (TMS) as an internal standard. Thermogravimetric analyses (TGA) were carried out on a V5.1A Dupont 2000 TGA analyser. X-ray diffraction (XRD) patterns were obtained on a Rigaku (Japan) X-ray Diffractometer (CuKα, = 1.5406 Å, Ni filter). Elemental analyses were performed on a Perkin Elmer 2400 CHN Elemental Analyser. Sodium analyses were carried out on a Digital Flamephotometer, Model CI 22 D (Elco Pvt. Ltd., India) with Na/K filter. The conductivity of the polymers was measured by the standard four-point probe method on pressed pellets of about (5 x 1 mm) dimensions.

Pyrrole (SRL, India) was distilled and kept under nitrogen atmosphere before use. 2,4-Dimethylpyrrole (97%), 1,3-propane sultone (98%) and squaric acid (98%) were purchased from Aldrich and were used without further purification. Lithium perchlorate was dried at 90 °C under vacuum for 24 h. All other reagents and solvents were locally purchased and purified according to literature procedures, wherever it was necessary.

3.4.1. Preparation of sodium 3-(pyrrol-1-yl)propane sulfonate (8)

To a suspension of NaH (0.02 mol, 50% suspension in paraffin oil) in dry DMSO (10 mL) under constant stirring and nitrogen atmosphere was slowly added pyrrole (1.34 g, 20 mmol) in DMSO (20 mL) at 60 °C over a period of 1 h. To this, 20 mmol (2.44 g) of 1,3-propane sultone was added dropwise and the reaction mixture was stirred at 60 °C for 2 h. Addition of acetone precipitated a solid product which was filtered, washed with hot THF to remove any unchanged sultone and dried in a vacuum oven at 60 °C for 24 h to give 3.2 g (76%) of **8** as a white solid , mp 200-210 °C (decomp.). IR ν_{max} (KBr) 3590, 3137, 3110, 2962, 2890, 1629, 1578, 1504, 1455, 1380, 1285, 1204, 971, 727, 609 cm^{-1}; ^{1}H NMR (DMSO-d_6, 90 MHz) δ 1.7-2.0 (2 H, m, CH_2), 2.29 (2 H, t, J = 6.9 Hz, CH_2), 3.77 (2 H, t, J = 7.2 Hz, $N\text{-}CH_2$) 5.79 (2 H, t, J = 2.1 Hz, aromatic), 6.53 (2 H, t, J = 2.1 Hz, aroamatic); ^{13}C NMR (DMSO-d_6, 22.5 MHz) 27.62, 47.73, 48.42, 107.58, 120.65; Anal. calcd for $C_7H_{10}NSNaO_3$: C, 39.81; H, 4.74; N, 6.64; S, 11.51; Na, 10.9. Found: C, 39.69; H, 4.75; N, 6.62; Na, 10.67.

3.4.2. Preparation of sodium 3-(pyrrol-1-yl)propane sulfonate-co-squaric acid (10)

A flask equipped with an azeotropic reflux condenser was charged with 1-butanol (20 mL), benzene (10 mL), 0.31 g (1.5 mmol) of **8** and 0.17 g (1.5 mmol) of **9** under nitrogen atmosphere. The reaction mixture was refluxed for 24 h with azeotropic removal of water. It was then cooled and benzene was evaporated under reduced pressure. The residual mass was treated with chloroform (200 mL) and the precipitated product was washed several times with 1-butanol. It was redissolved in methanol and reprecipitated from chloroform. The precipitate was collected by filtration, washed several times with chloroform and dried in a vacuum oven at 40 °C for 24 h to give 390 mg (86%) of **10.** IR ν_{max} (KBr) 3519, 2941, 1725, 1650, 1564, 1198, 1053, 732, 611 cm^{-1}; UV λ_{max} (DMSO) 574, 612 nm; λ_{max} (H_2O) 562 and 597 nm; ^1H NMR (DMSO-d_6, 90 MHz) δ 1.5-1.85 (2 H, m, CH_2), 2.2 (2 H, t, S-CH_2), 4.65 (2 H, t, NCH_2), 6 (1 H, s, br, aromatic), 6.85 (1 H, s, br, aromatic); ^{13}C NMR (DMSO-d_6, 22.5 MHz) δ 18.49, 26.79, 27.63, 48.42, 56.03, 79.15, 100.42, 107.37, 120.47, 151.38, 157.86; Anal. calcd for $(C_{11}H_8NSNaO_5)_n$: C, 45.67; H, 2.77; N, 4.84; S, 11.07; Na, 7.96. Found: C, 45.30; H, 2.62; N, 4.61; Na, 8.28.

3.4.3. Preparation of sodium 3-(2,4-dimethylpyrrol-1-yl)propane sulfonate (13)

Compound **13** (2.1 g, 88%), mp 160-170 °C (dec.) was synthesized from 0.95 g (10 mmol) of 2,4-dimethylpyrrole and 1.22 g (10 mmol) of 1,3-propane sultone, employing the same procedure adopted for **8**. IR ν_{max} (KBr) 3609, 3529, 2981, 2934, 1695, 1625, 1528, 1418, 1210, 1063, 783, 734, 608 cm^{-1}; ^1H NMR

(DMSO-d_6, 90 MHz) δ 1.6-1.9 (8 H, m, CH_3, CH_2), 1.95 (2 H, s, CH_3), 2.35 (2 H, t, J = 7.6 Hz, CH_2), 3.69 (2 H, t, J = 7.2 Hz, N-CH_2), 5.43 (1 H, s, aromatic), 6.25 (1 H, s, aromatic); ^{13}C NMR (DMSO-d_6, 22.5 MHz) δ 11.78, 12.11, 27.24, 44.69, 48.48, 108.9, 115.70, 117.9, 127.42; Anal. calcd for $C_9H_{14}NSNaO_3$: C, 45.18; H, 5.86; N, 5.86; S, 13.39; Na, 9.62. Found: C, 45.30; H, 5.82; N, 5.81; Na, 9.92.

3.4.4. Preparation of model dye 14

A mixture of 0.48 g (2 mmol) of **13**, 0.11 g (1 mmol) of **9**, 20 mL of 1-butanol and 10 mL of benzene was refluxed for 6 h under nitrogen and the water formed was removed azeotropically. The reaction mixture was cooled, and benzene was removed under vacuum. This mixture was poured into chloroform (200 mL) and the precipitated product was filtered, dried and then dissolved in methanol. The solution was filtered and the filtrate was poured into chloroform (300 mL). The precipitated dye was filtered, dried and then redissolved in DMSO. The DMSO solution was poured into excess of chloroform, and the precipitated dye was filtered, washed several times with chloroform and dried in a vacuum oven at 50 °C for 24 h to give 0.41 g (73%) of **14**. IR ν_{max} (KBr) 3423, 2933, 1654, 1620, 1510, 1455, 1397, 1349, 119, 1123, 1048, 975 cm^{-1}; UV λ_{max} (DMSO) 584 nm, λ_{max} (H_2O) 562 nm; ^1H NMR (DMSO-d_6, 90 MHz) δ 1.7–1.95 (4 H, m, CH_2), 2.3 (6 H, s, CH_3), 2.45-2.75(10 H, m, CH_3, SCH_2), 4.75 (4 H, t, NCH_2), 6.25 (2 H, s, aromatic); ^{13}C NMR (DMSO-d_6, 22.5 MHz) δ 27.45, 43.14, 48.12, 119.07, 126.23, 137.48, 147.77, 174.21, 175; Anal. calcd for $C_{22}H_{26}N_2S_2Na_2O_8$: C, 47.48; H, 4.68; N, 5.03; S, 11.51; Na, 8.27; O, 23.02. Found: C, 47.32; H, 4.73; N, 5.23; Na, 8.04.

3.4.5. Preparation of the random oligomers 15a-d

The random oligomers **15a-d** were prepared adopting methods similar to the synthesis of the oligomer **10**. Analytical results and spectral data of the oligomers **15a-d** are summarized below.

15a: (58%); M_n, 3800; IR ν_{max} (KBr) 3406, 2940, 1728, 1588, 1556, 1488, 1288, 1045, 944, 803, 745 cm^{-1}; UV λ_{max} (DMSO) 556, 628, 720 nm; λ_{max} (H_2O) 525, 580 nm; ^{1}H NMR (DMSO-d_6, 90 MHz) δ 1.45–1.85 (2 H, m, CH_2), 2.2 (2 H, t, S-CH_2), 4.7 (2 H, t, N-CH_2), 5.75-5.8 (s, br, aromatic), 6.6-6.9 (s, br, aromatic); Anal. calcd for $(C_8H_3NO_2)_{4n}$+$(C_{11}H_8NSNaO_5)_n$: C, 59.38; H, 2.3; N, 8.05; S, 3.68; Na, 2.65. Found: C, 62.71, H, 2.19; N, 8.84; Na, 1.86.

15b: (62%); M_n, 3860; IR ν_{max} (KBr) 3405, 2939, 1788, 1724, 1586, 1563, 1489, 1186, 1046, 945, 737 cm^{-1}; UV λ_{max} (DMSO) 555, 628, 726 nm; λ_{max} (H_2O) 534, 600 nm; ^{1}H NMR (DMSO-d_6, 90 MHz) δ 1.45–1.85 (2 H, m, CH_2), 2.2 (2 H, t, CH_2-SO_3), 4.7 (2 H, t, N-CH_2), 5.75-5.8 (s, br, aromatic), 6.6-6.9 (s, br, aromatic); Anal. Calcd for $(C_8H_3NO_2)_{3n}$+$(C_{11}H_8NSNaO_5)_{2n}$: C, 54.49; H, 2.47; N, 6.91; S, 6.32; Na, 4.54. Found: C, 58.06; H, 2.35; N, 7.76; Na, 3.41.

15c: (64%); M_n, 3850; IR ν_{max} (KBr) 3458, 2939, 1781, 1723, 1670, 1569, 1488, 1191, 1045, 805, 735 cm^{-1}; UV λ_{max} (DMSO) 561, 615, nm; λ_{max} (H_2O) 595 nm; ^{1}H NMR (DMSO-d_6, 90 MHz) δ 1.45–1.85 (2 H, m, CH_2), 2.2 (2 H, t, CH_2-SO_3), 4.7 (2 H, t, N-CH_2), 5.75-5.8 (s, br, aromatic), 6.6-6.9 (s, br, aromatic); Anal. calcd for $(C_8H_3NO_2)_{2n}$+$(C_{11}H_8NSNaO_5)_{3n}$: C, 50.82; H, 2.59; N, 6.05; S, 8.29; Na, 5.96. Found: C, 54.44; H, 2.47; N, 6.90; Na, 4.57.

15d: (74%) M_n, 3900; IR ν_{max} (KBr) 3526, 3402, 1780, 1583, 1480, 1306, 1047, 814, 714 cm^{-1}; UV λ_{max} (DMSO) 560, 623 nm; λ_{max} (H_2O) 540, 595 nm; ^{1}H NMR

(DMSO-d_6, 90 MHz) δ 1.45–1.85 (2 H, m, CH_2), 2.2 (2 H, t, CH_2-SO_3), 4.7 (2 H, t, N-CH_2), 5.75-5.8 (s, br, aromatic), 6.6-6.9 (s, br, aromatic); Anal. calcd for $(C_8H_3NO_2)_n$+$(C_{11}H_8NSNaO_5)_{4n}$: C, 47.96; H, 2.69; N, 5.38; S, 9.84; Na, 7.07; O, 27.05. Found: C, 52.24; H, 2.55; N, 6.39; Na, 6.36.

3.5. References

1. Patil, A. O.; Ikenoue, Y.; Basescu, N.; Colneri, N.; Chen, J.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1987**, *20,* 151.
2. Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858.
3. Ikenoue,Y.; Chiang, J.; Patil, A. O.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1988**, *110*, 2983.
4. Ikenoue,Y.; Uotani, N.; Patil, A. O.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1989**, *30*, 305.
5. Ikenoue,Y.; Saida,Y.; Kira, M.; Tomozawa, H.; Yashima, H.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1694.
6. Chen, S.-A.; Hua, M. -Y. *Macromolecules* **1993**, *26*, 7108.
7. Arroyo, M. I.; Diaz-Quijada, G. A.; Abdou, M. S. A.; Holdcroft, S. *Macromolecules* **1995**, *28*, 975.
8. Chen, S.-A.; Hua, M. -Y. *Macromolecules* **1996**, *29*, 4919.
9. Sundaresan, N. S.; Basak, S.; Pomerantz, M.; Reynolds, R. *J. Chem. Soc., Chem. Commun.* **1987**, 621.
10. Havinga, E. E.; van Horssen, L.W.; ten Hoeve, W.; Wynberg, H.; Meijer, E. W. *Polym. Bull.* **1987**, *18*, 277.
11. Havinga, E. E.; ten Hoeve,W.; Meijer, E. W.; Wynberg, H. *Chem. Mater.* **1989**, *1*, 650.
12. Yue, J.; Epstein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 2800.
13. Yue, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. J.; MacDiarmid, A. G. *J. Am. Chem. Soc.* **1991**, *113*, 2665.
14. Bergeron, J. Y.; Chevalier, J. W.; Dao, C. H. *J. Chem. Soc., Chem. Commun.* **1990**, 180.

15. Chen, S.-A.; Hwang, Gue. W. *J. Am. Chem. Soc.* **1994**, *116*, 7939.
16. Ng, S. C.; Chan, H. S. O.; Huang, H. H.; Ho, P. K. H. . *J. Chem. Soc., Chem. Commun.* **1995**, 1327.
17. Chan, H. S. O.; Huang, H. H.; Ho, P. K. H.; Ng, S. C.; Tan, B. T. G.; Tan, K. L. *J. Am. Chem. Soc.* **1995**, *117*, 8517.
18. Vachon, D. J.; Angus, R. O., Jr.; Lu, F. L.; Nowak, M.; Liu, Z. X.; Schaffer, H.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1987**, *18*, 297.
19. Wudl, F.; Angus, R. O., Jr.; Lu, F.L.; Allemand, P. M.; Vachon, D. J.; Nowak, M.; Liu, Z. X.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3677.
20. Hall, H. K., Jr.; Padias, A. B.; Williams, P.A.; Gosau, J.-M.; Boone, H. W.; Park, D.-K. *Macromolecules*, **1995**, *28*, 1.
21. Boone, H. W.; Hall, H. K., Jr. *Macromolecules*, **1996**, *29*, 5835.
22. Treibs, A.; Jacob, K. *Angew.Chem., Int. Ed. Engl.* **1965**, *4*, 694.
23. Treibs, A.; Jacob, K. *Justus Liebigs Ann. Chem.* **1966**, *699*, 153.
24. Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie, Weinheim, Germany, **1979**.
25. Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.
26. Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485.
27. Kamlet, M. J.; Abboud, J. -L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.
28. Das, S.; Thomas, K. G.; Ramanathan, R.; George, M.V.; Kamat, P.V. *J. Phys. Chem.* **1993**, *97*, 13625.
29. Dirk, C. W.; Herndon, W. C.; Cervantes-Lee, F.; Selnau, H.; Martinez, S.; Kalamegham, P.; Tan, A.; Campos, G.; Velez, M.; Zyss, J.; Ledoux, I.; Cheng, L.-T. *J. Am.Chem. Soc.* **1995**, *117*, 2214.

30. Hotta, S.; Rughooputh, D. D. V.; Heeger, A. J. *Synth. Met.* **1987**, *22*, 79.
31. Inganas, O.; Gustafsson, G. *Synth. Met.* **1990**, *37*, 195.
32. Wang, H. L.; Toppare, L.; Fernandez, E. *Macromolecules* **1990**, *23*, 1053.
33. Chen, S.-A.; Fang, W-G. *Macromolecules* **1991**, *24*, 1242.

CHAPTER 4

SYNTHESIS AND STUDIES OF OLIGOSQUARAINE DYE BASED METAL ION SENSORS

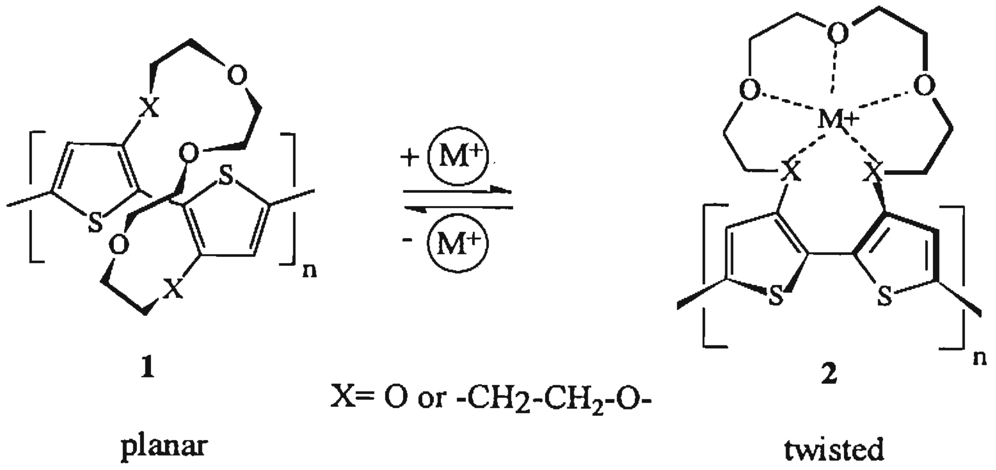
4.1. Introduction

Studies of molecular recognition between receptors and substrates (host-guest) have gained considerable attention in recent years due to their fundamental and technological importance[1]. Several molecule-based sensory devices based on the principle of molecular recognition are reported in the literature[2,3]. A molecule based practical sensory device must efficiently transduce molecular interactions into a readily measurable response. In order to achieve this, one has to append to the receptor framework, a molecular subunit which exhibits distinct properties, upon receptor-substrate interaction. In other words, a molecule-based sensory device requires molecular recognition events occurring at receptors which have been designed to exhibit different properties before and after the recognition events.[4]

The role of the sensing agent in a chemical sensor is to provide a transduction mechanism which enables to produce a measurable analytical signal. The majority of the receptors investigated as potential chemical sensors have employed either electrochemical or optical transduction mechanisms. Among these methods, the optical transduction mechanism, particularly the changes associated with the optical absorption and emission properties, are the easiest and simplest to measure. Crown ether attached organic dye molecules are established examples of optical sensory materials. The increased sensitivity in such systems requires an increase in the binding energy between receptor and guest molecules which in turn should produce considerable perturbation to their physical properties such as optical absorption or emission. Unfortunately, such an approach to enhance sensitivity can have the disadvantage of irreversible response or very long reset times. An additional limitation may be the non availability of receptors with sufficiently high association constants. In this context, the use of conjugated polymer based fluorescent sensors have great significance.

Recent advances in the synthesis and studies of π-conjugated conducting polymers have led to the design of macromolecular wires with tailored properties. Several applications of such materials in single molecule photovoltaic devices and molecular electronics have now been realized.[5-8] It is well-known that changes in the coplanarity of a π-conjugated polymer backbone can result in a sharp drop in its conductivity,[9] Several people have exploited this property in the designing of conducting polymer-based metal ion sensors.[10-13]

Recently, Marsella *et al.* have reported the synthesis and properties of several crown ether substituted polythiophenes which are ideal choice in the designing of sensory materials due to their ease of structural modification.[14-18] A representative example of a polythiophene based metal ion sensor is shown in Scheme 1. Several macromolecular sensors based on polythiophene have been reported in the literature and some of these structures are shown in Chart 1. The chemoresistive polymer **3** derived from a bithiophene containing cyclophane receptors are capable of forming self-assembled pseudorotaxane complexes with paraquat.[19] The electrostatic perturbations arising from psuedo-polyrotaxane formation cause a decrease in carrier mobility of the electrical charges thereby lowering the conductivity. The polymer **4** represents an ionoresistive polythio-



Scheme 1

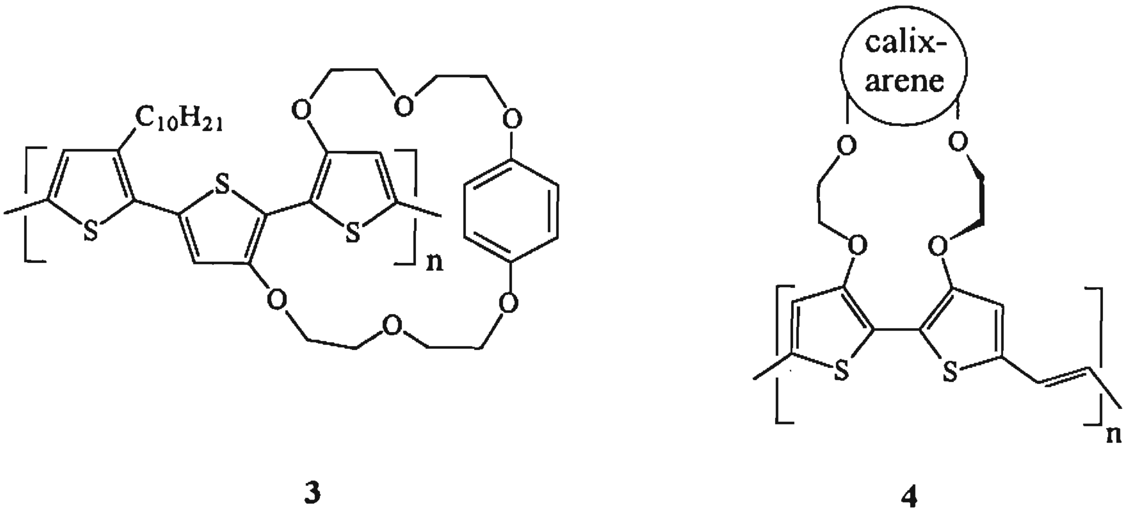
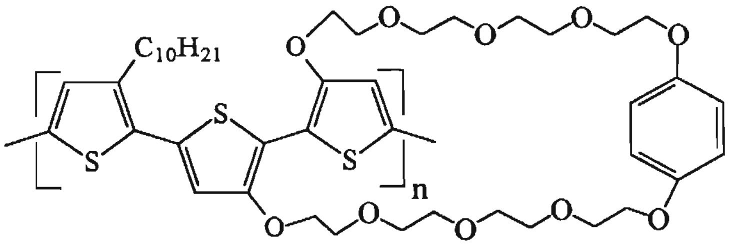


Chart 1

phene functionalized with calix[4]arene based ion receptors.[20] This polymer shows ion selective voltammetric, chromic and resistive responses which makes it ideal as polymer based sensory material. Although, the calix[4]arene substituted polythiophene exhibits only minimal changes in the UV-Vis spectrum and voltammetric responses, a large decrease in its conductivity could be achieved, on exposure to alkali metal ions.

Despite the reports of polythiophene based chemoresistive and ionoresistive macromolecular sensors, polymer based metal ion sensors in which the transduction mechanism is achieved through the response in their optical absorption or emission are rather limited. This could probably be due to the difficulties associated with the choice of soluble π-conjugated polymeric systems having suitable optical properties in the visible region. Recently, Marsella *et al.* have reported the synthesis of several fluorescence chemosensors, two representative examples of which are shown in Chart 2.[21,22] The molecular wires **5** and **6** interconnected with cyclophane based receptors lead to fluorescent chemosensors having enhanced sensitivity relative to a single receptor sensory molecule **7**. The origin of this effect is attributed to the facile energy migration through the conjugated polymer backbone which is a property of the collective system rather than those of the discrete units of the polymer.

Levesque and Leclarc[23] have synthesized a polymeric sensor **8** which shows ionochromic and thermochromic responses. The low bandgap zwitterionic polymer **9** reported by Brockmann and Tour[24,25] is an example of a polymeric sensor in which the metal ion recognition is achieved through the response in its optical



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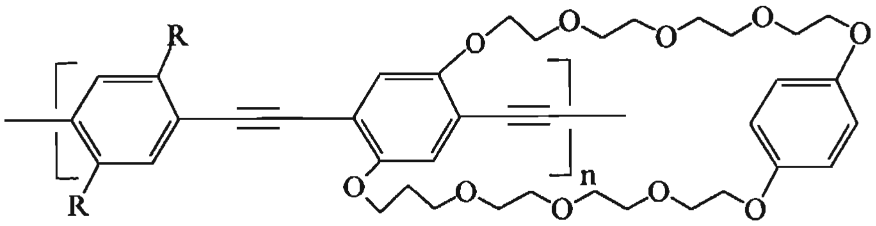
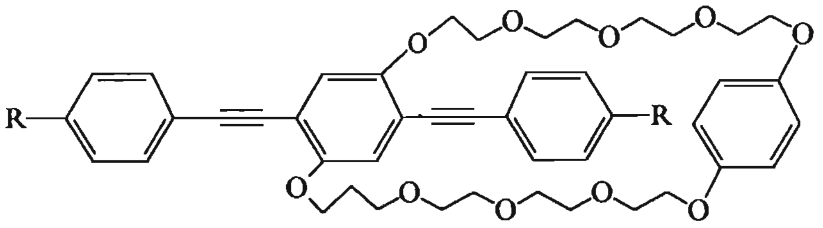


R = CON(C_8H_{17})$_2$

6

Chart 2



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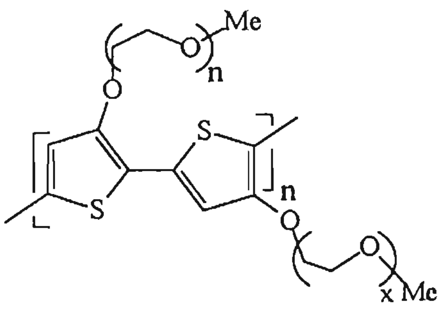
absorption changes. The presence of the oxyethylene subunits and their chain lengths are critical for the dramatic ionochromic responses of polymers **8** and **9**. Since, the sensitivity of metal ion recognition based on the perturbation in the fluorescence emission, is much better than the sensitivity associated with the changes in the optical absorption, metal ion sensors based on the former phenomenon is preferred over the later.



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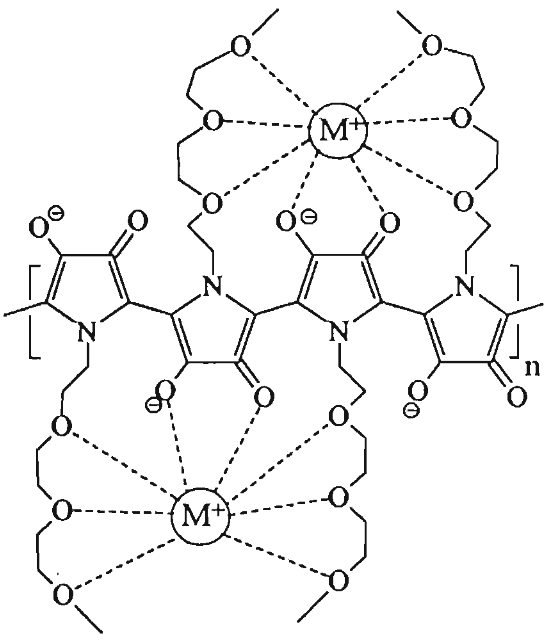

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Chart 3

Fluorescence quenching property of crown ether appended organic dyes such benzoxazinones[26,27], coumarins[28], stilbenes[29] and styrylpyridines[30] have been extensively used in the designing of several fluoroionophores for the detection of various metal ions. Recently Das *et al.* have synthesized several azacrown attached squaraine fluoroionophores **10** (Chart 4) for alkali metal ion detection. Squaraine dye based metal ion sensors have the advantage of having intense absorption and emission in the visible region. Due to the ease of synthetic procedure and excellent optical properties of squaraine dyes, we thought of designing π-conjugated macromolecular squaraine dyes for the detection of alkali metal ions. Such molecular wire based sensors derived from squaraine dyes are expected to show enhanced sensitivity for metal ion detection compared to simple squaraine dyes. In the present study, squaraine dye based oligomers (molecular wires) containing pendent oxyethylene chains have been synthesized and their optical and metal ion sensing properties have been evaluated.

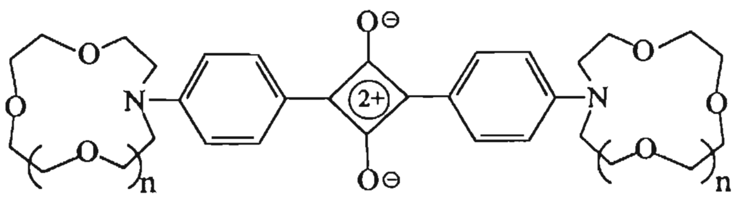

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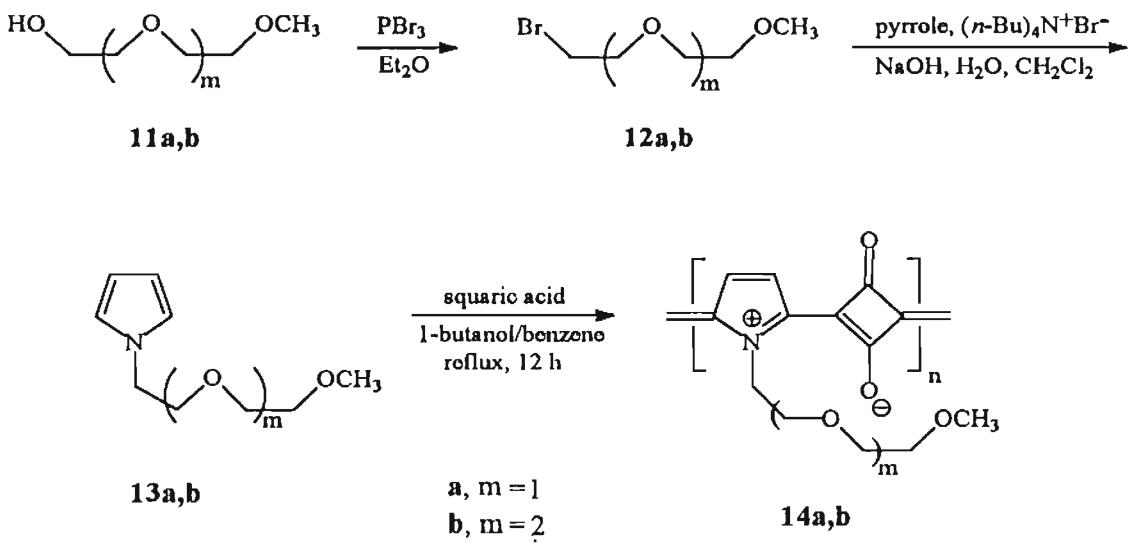
Chart 4

4.2. Results and Discussion

4.2.1. Synthesis of squaraine dye based molecular wires containing pendent oxyethylene chains (14a,b)

The synthetic route for **14a** and **14b** is shown in Scheme 2. The bromo derivatives of triethylene glycol monomethyl ether **12a** and tetraethylene glycol monomethyl ether **12b** were prepared by the reaction of phosphorous tribromide with the corresponding glycols **11a** and **11b** in 71% and 67% yields, respectively. The N-[methoxyethoxy)ethyl]pyrrole **13a** and N-[[(methoxyethoxy)ethoxy]-ethyl]pyrrole **13b** were obtained by the reaction of pyrrole with **12a** and **12b** in 67% and 64% yields, respectively. The polycondensation reaction between the pyrrole derivatives **13a** and **13b** with squaric acid were carried out in a 1:1 mixture of 1-butanol and benzene, under azeotropic reflux conditions. The solvents were



Scheme 2

removed partially and the viscous blue solution obtained in each case was poured into petroleum ether to get a pasty solid. This was redissolved in the minimum amount of DMSO and reprecipitated from petroleum ether. The precipitate was collected by filtration and washed several times with diethyl ether and extracted with methanol and chloroform. The combined extracts were evaporated under vacuum to give 62% of **14a** and 56% **14b**. The molecular weights of **14a** and **14b** were determined by gel permeation chromatography which showed a number average molecular weight of approximately 1800 atomic mass units. This corresponds to molecular wires consisting of an average of four squaraine dye units each separated by an alternate C_2O_4 moiety.

The IR spectra of the products **14a** and **14b** showed a strong absorption peak of the cyclobutane 1,3-diolate moiety around 1620 cm^{-1} in each case. This is characteristic of the resonance stabilized zwitterionic structure of squaraine dyes in general. The ^1H NMR spectra of **14a** (Figure 1) in $CDCl_3$ showed a multiplet around δ 3.35-3.8 corresponding to the oxyethylene side chains. The CH_2 protons attached to the pyrrole nitrogen appeared as a broad triplet around δ 4.8. The two aromatic protons of the pyrrole ring appeared as a broad singlet round δ 6.2. The

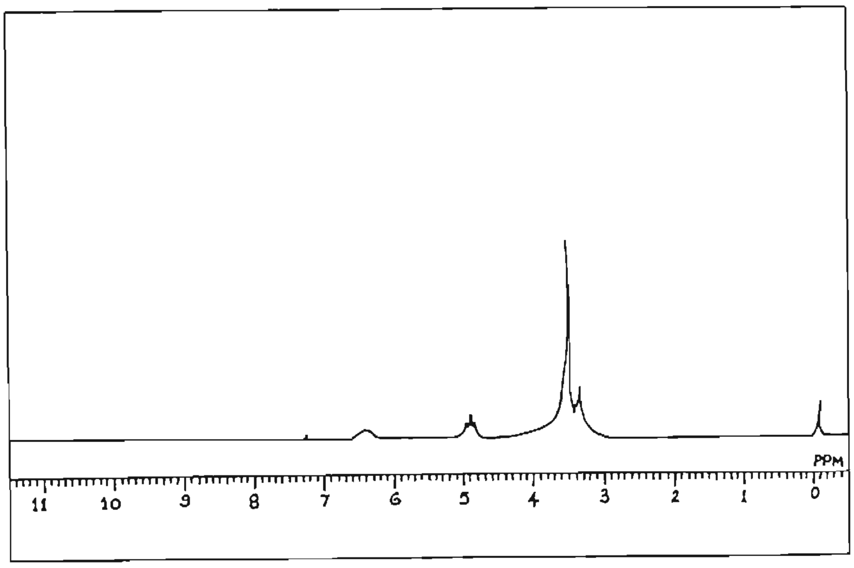
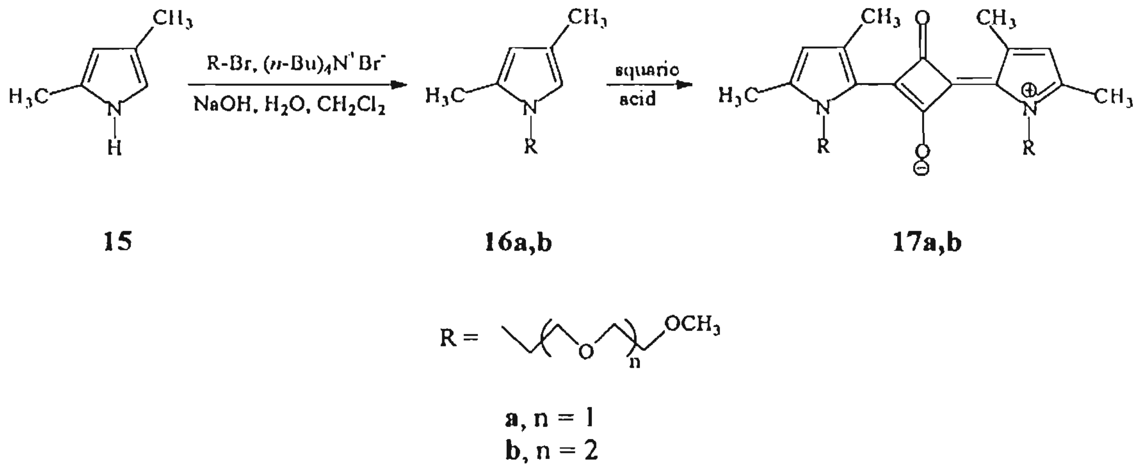


Figure 1. ^1H NMR spectrum of **14a**.

^1H NMR spectrum of **14b** was also in agreement with its structure. The ^{13}C NMR spectra of **14a** and **14b** were poorly resolved due to their low solubility in $CDCl_3$. The primary and secondary carbon atoms of the oxyethylene chains appeared between 42-72 ppm in both cases, whereas the tertiary and quaternary carbon atoms could not be resolved. Comparison of the spectral properties of **14a** and **14b** with those of the various macromolecular squaraines reported in earlier chapters showed similarities except in their side chain groups, indicating a zwitterionic structure of **14a** and **14b**.

4.2.2. Preparation of the model squaraine dyes 17a and 17b

The model squaraine dyes **17a** and **17b** were prepared as per Scheme 3 for comparing their spectral characteristics and physical properties with those of the molecular wires **14a** and **14b**. The pyrrole derivatives **16a** and **16b** were obtained in 67% and 64%, respectively by the reaction of 2,4-dimethylpyrrole and the corresponding bromoderivatives in the presence of sodium hydride in DMF.



15 **16a,b** **17a,b**

a, n = 1
b, n = 2

Scheme 3

Condensation of squaric acid with **16a** and **16b** in 1-butanol-benzene mixture (1:1), under azeotropic removal of water gave **17a** and **17b** in 67% and 64% yields, respectively. These compounds were purified by crystallization from a mixture of dichloromethane and petroleum ether (1:2) to give bright greenish crystals.

The IR spectra of both **17a** and **17b** showed strong absorptions around 1605 cm^{-1} which are characteristic of the C-O stretching frequency of the cyclobutane-1,3-diolate moiety. The IR spectra of **17a** and **17b** are comparable to those of **14a** and **14b**, indicating their structural similarity. The ^1H NMR spectrum of **17a** showed two singlets at δ 2.35 and 2.63, corresponding to the four CH_3 groups attached to the two pyrrole moieties (Figure 2). The protons attached to the OCH_3 groups appeared as a singlet at δ 3.29. The multiplets around δ 3.42 correspond to eight protons which are assigned for protons of the oxyethylene groups. Two triplets at δ 3.67 and 4.85 are observed which are equivalent to four protons each. These are assigned for one set of OCH_2 and NCH_2 groups each. The aromatic protons of the two pyrrole rings appeared as a singlet at δ 6.0. The ^{13}C NMR spectrum (Figure 3) of **17a** showed a total of 13 carbon signals which is exactly half of the total number of 26 carbon atoms present, which indicates that each half of the molecule is identical. The two carbon signals at 13.75 and 15.18 ppm correspond to the four CH_3 groups, attached to the pyrrole moieties. The signals at δ 47.16, 58.86, 70.46, 71.80 and 71.98 ppm were assigned for the ten carbon atoms of the two oxyethylene moieties. The four signals appeared at 117.72. 126.61, 139.26 and 148.51 were due to the eight carbon atoms of the two pyrrole rings. Two signals at 173.96 and 176.29 were observed for the four carbon atoms of the central C_2O_4 moiety. The IR and NMR spectral analyses reveal that **17a** has a resonance stabilized zwitterionic structure. The NMR spectrum of the squaraine

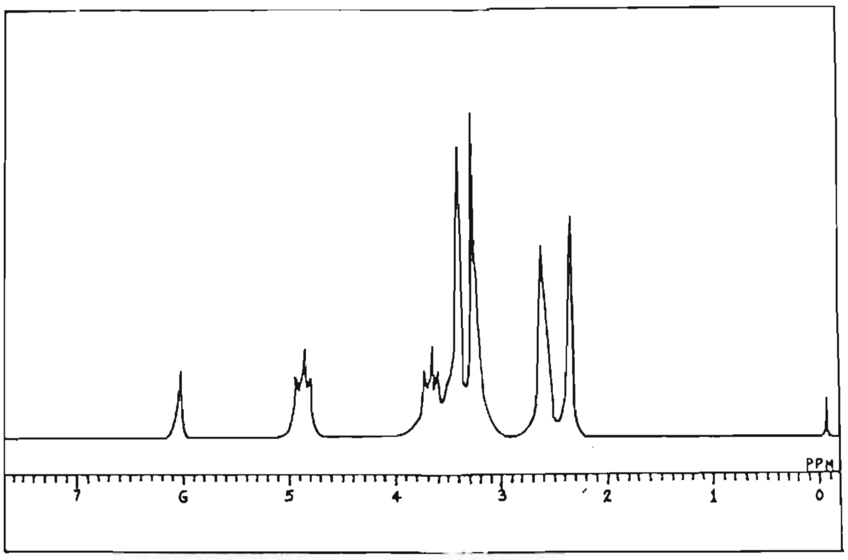


Figure 2. ^{1}H NMR spectrum of **17a**.

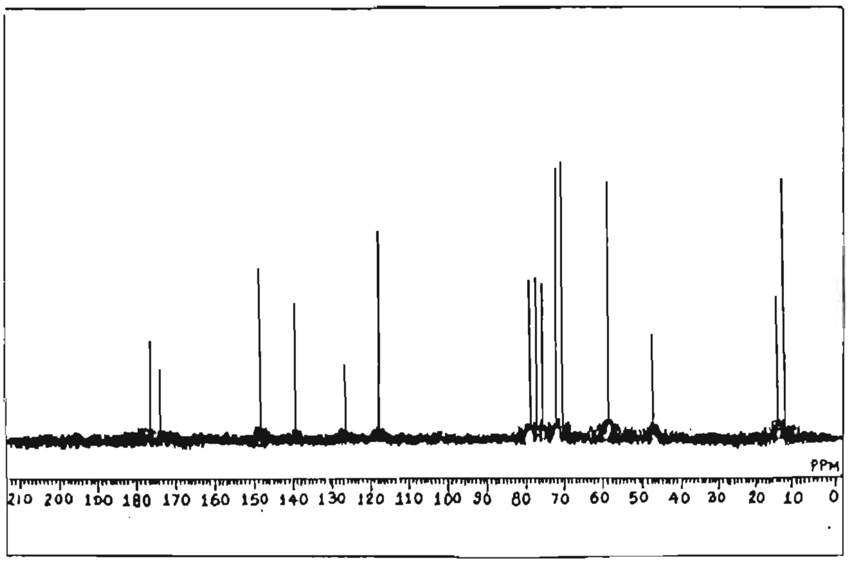


Figure 3. ^{13}C NMR spectrum of **17a**.

dye **17b** also agrees with its proposed structure. Comparison of the NMR spectral data of **17a** and **17b** with those of the squaraine molecular wires **14a** and **14b** reveals that all these molecules have structural similarities to each other.

4.2.3. Absorption and emission properties of 14a,b and 17a,b

The absorption spectra of **14a** and **17a** in DMSO are shown in Figure 4. The model squaraine dye **17a** showed an intense sharp absorption maximum at 583 nm whereas the oligosquaraine dye **14a** showed a broad absorption with two maxima around 564 nm with a shoulder around 602 nm. The broad spectrum of

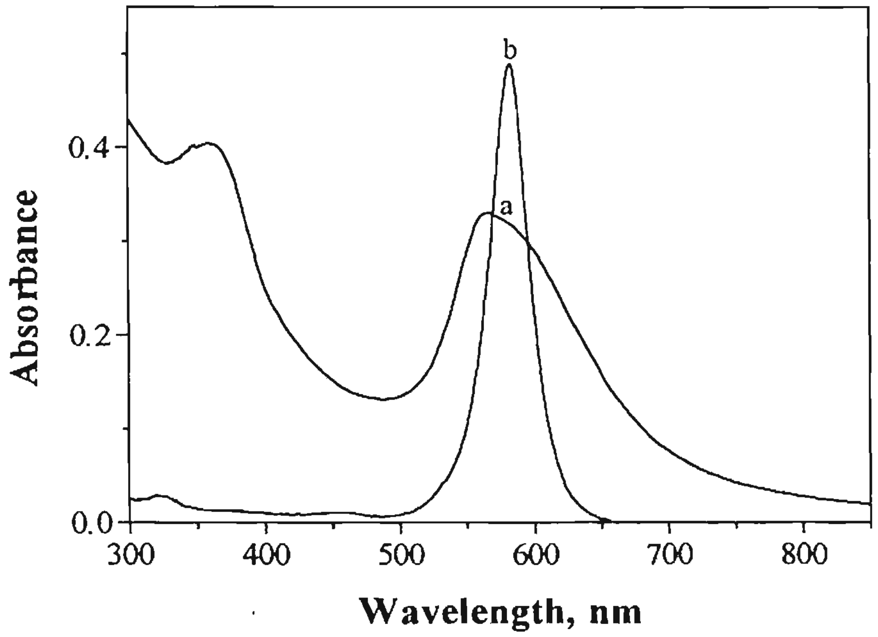


Figure 4. UV-Vis absorption spectra of (a) **14a** and (b) **17a** in DMSO.

14a compared to the sharp and intense absorption of **17a** reveals the macromolecular nature of **14a**. The blue shifted absorption of **14a** despite of its extended conjugation compared to **17a** can be attributed to the presence of four methyl groups in **17a**. The presence of methyl groups in the pyrrole moieties make them strong electron donors thereby enhancing the charge-transfer interaction in **17a** compared to **14a**. Similar observations were made during the synthesis of the polysquaraines described in Chapters 2 and 3 which were not pursued due to their lack of importance with respect to the conductivity studies. The optical absorption spectra of **14b** and **17b** were identical to those of **14a** and **17a**.

The fluorescence emission spectra of **14a** and the model squaraine dye **17a** in DMSO are compared in Figure 5. The fluorescence emission of **17a** showed a

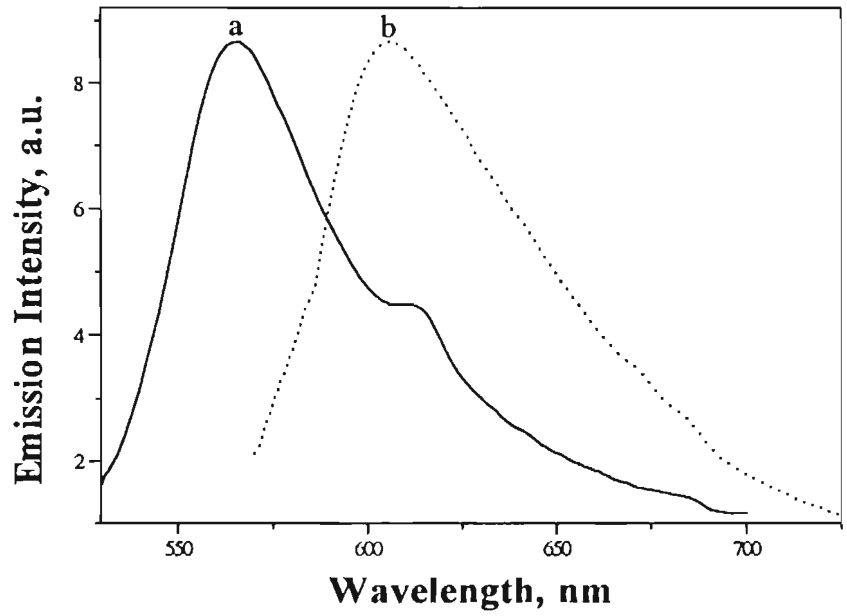


Figure 5. Emission spectra of (a) **14a** and (b) **17a** in DMSO.

maximum around 606 nm with a Stoke shift of nearly 23 nm whereas **14a** showed an emission maximum of 574 nm with a Stoke shift of only 9 nm. This could be due to the relatively rigid framework of **14a**, compared to **17a**. The macromolecular squaraine dye **14b** showed an emission maximum of 575 nm with a Stoke shift of 11 nm. Despite the rigid structures of **14a** and **14b**, their fluorescence quantum yields (Φ_f) in DMSO were very low probably due to the self-quenching process which can be due to strong association of the macromolecular chains.

The absorption spectra of **14a,b** and **17a,b** in alcoholic solvents showed blue shifts with increase in hydrogen bonding ability of the solvents. Since there were no significant differences between the absorption properties of **14a** and **14b** and also between **17a** and **17b** in various solvents used, **14a** and **17a** were chosen as representative systems for further detailed studies. The changes in the UV-Vis absorption spectra of **14a** and **17a** in various alcoholic, hydrogen bonding solvents are shown in Figures 6 and 7. The observed negative solvatochromism of **14a** and **17a** in alcoholic solvents is attributed to specific solute-solvent hydrogen bonding interaction. The strength of such interaction is expected to depend upon the relative acidity of the solvents. This is evident from the linear relationship observed for **14a** and **17a** when their absorption maxima in wavenumbers are plotted against the acidity parameter, 'α' of the hydrogen bonding donor solvents (Figure 8).

Addition of small amounts of 2,2,2-trifluoroethanol (TFE), which is a strongly hydrogen bonding solvent, brought about shifts in the absorption maxima of **14a** and **17a**, to the blue region. With increasing concentration of TFE, the

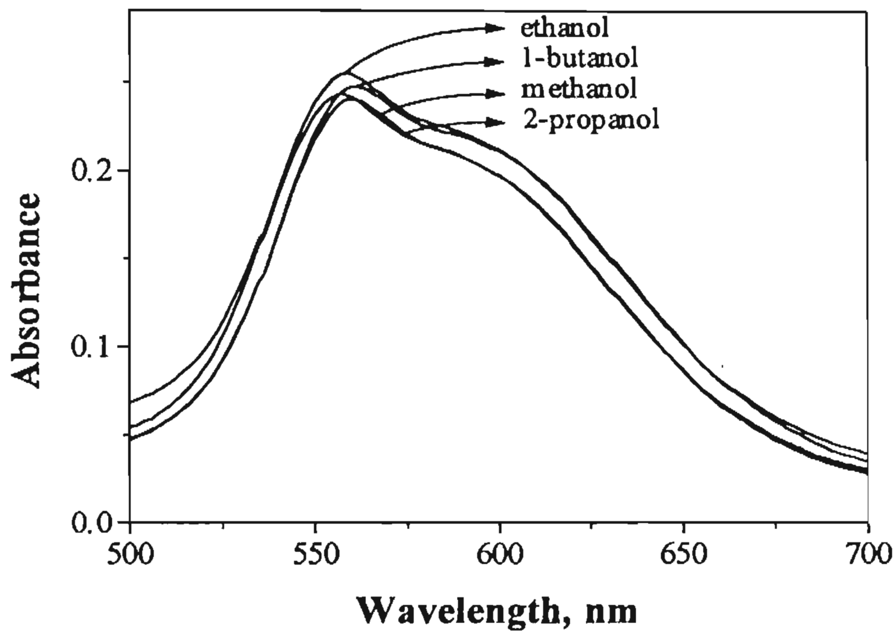


Figure 6. Absorption spectra of **14a** in various alcoholic solvents.

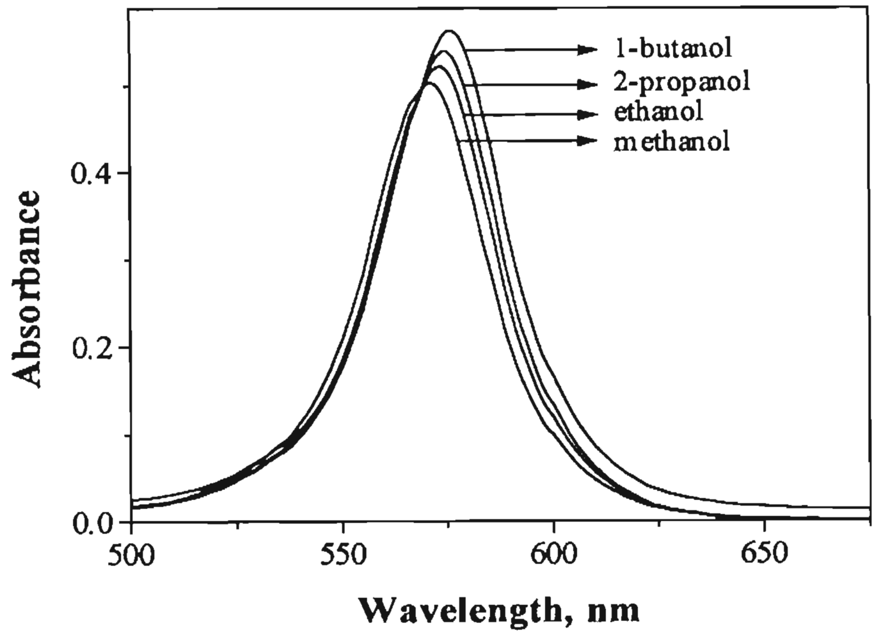


Figure 7. Absorption spectra of **17a** in various alcoholic solvents.

absorption spectrum, in each case, shifted to shorter wavelengths, accompanied by a marginal increase in the intensity of absorption. Addition of equivalent amounts of polar, aprotic solvents such as acetonitrile to a solution of **14a** or **17a** did not change the absorption spectra. The substantial changes in the absorption spectra observed upon addition of TFE further suggest the involvement of hydrogen bonding interaction between the solvent and the solute. TFE and related alcoholic solvents are known to form hydrogen bonded complexes with organic dye molecules.[32,33] In the present case, TFE may be forming hydrogen bonds with the negatively charged oxygen atoms of the central C_2O_4 moiety. Such an interaction

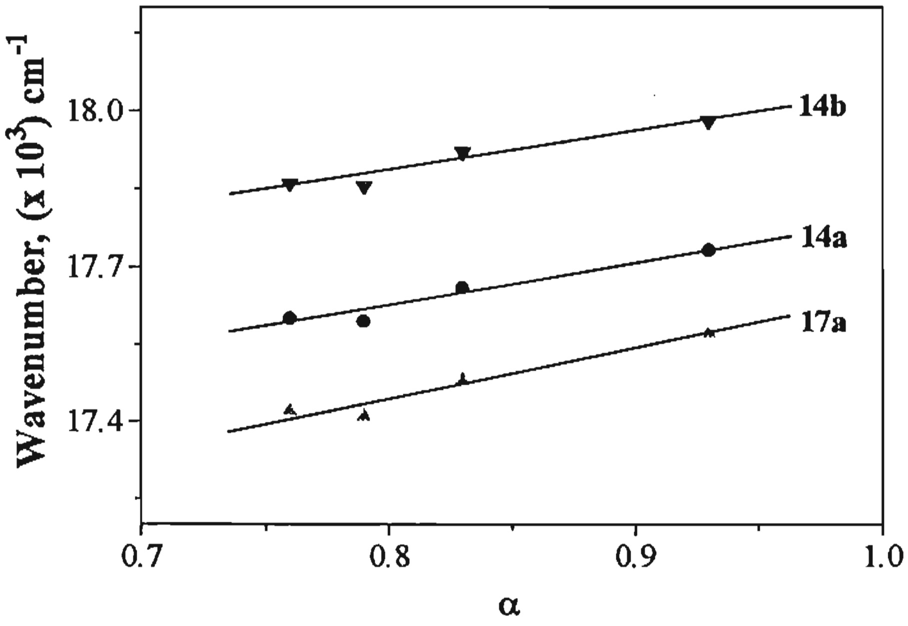


Figure 8. Plot of acidity parameter α versus UV-Vis absorption maxima of **14a,b** and **17a** in different solvents.

is expected to be strong in the ground state of the squaraines **14a** and **17a** due to their highly polar zwitterionic structures. The observed negative solvatochromic properties of **14a** and **17a** are comparable to those of several other squaraine dyes, as reported in the literature.[34,35]

4.2.4. Effect of alkali metal ion binding with 14a,b and 17a,b

The alkali metal ion sensing abilities of the squaraine molecular wires **14a** and **14b** and the model squaraine dyes **17a** and **17b** were studied making use of the changes in their absorption and emission properties upon metal ion binding. DMSO was used as the solvent for these studies due to the better solubility of **14a,b**, **17a,b** and the alkali metal ion salts under investigation. Even though **14a,b** and **17a,b** have similar optical spectral changes under various conditions, they behaved differently on alkali metal ion binding. These changes are highly specific for different alkali metal ions. For example, the absorption spectral changes of **14a** on addition of micromolar quantities of lithium perchlorate are shown in Figure 9. The intensity of absorption at 565 nm is significantly enhanced with a marginal red shift to 570 nm on addition of 10 μM of lithium perchlorate. On the other hand, the optical absorption spectra of **14b** containing the triethylene glycol monomethyl ether pendent groups did not show any noticeable change in its optical absorption spectrum upon addition of the same amount of lithium perchlorate solution. Similarly, addition of sodium perchlorate did not produce significant changes to the absorption spectra of any of the materials under investigation. However, addition of micromolar quantities of potassium perchlorate induced a slight change in the absorption of **14b**. These observations reveal that **14a** is selective towards lithium ions, whereas **14b** is sensitive to potassium ions. Both **14a** and **14b** did not show significant response to sodium ions. Interestingly, the model dyes **17a** and **17b** did not show significant sensing ability towards alkali metal ions.

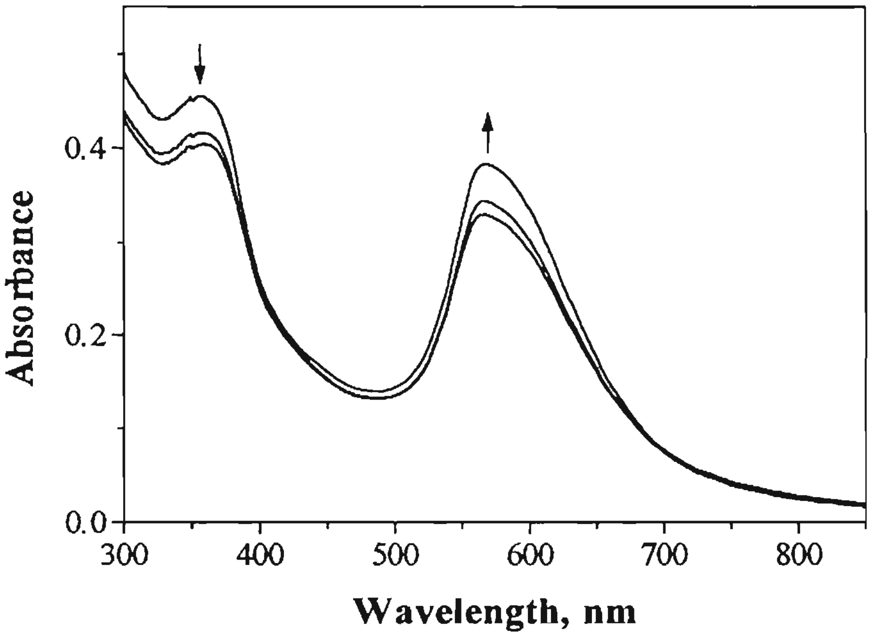


Figure 9. Effect of $LiClO_4$ (μM) on absorption spectrum of **14a**.

The selectivity in the metal ion sensing ability of the squaraine molecular wires has been further investigated using the more sensitive fluorescence emission spectroscopy. The emission spectral changes are known to be highly sensitive towards the metal ion complexation in the case of several organic dyes. It has been observed in the present study that the squaraine molecular wires **14a** and **14b** and their model compounds **17a** and **17b** show remarkable differences in their fluorescence emission behaviour upon complexation with alkali metal ions. The changes in the fluorescence spectrum of **14a** in DMSO upon addition of micromolar quantities of lithium perchlorate is shown in Figure 10. Significant enhancement in the intensity of emission was noticed in this case whereas, in the case of **14b** the effect was comparatively less. The molecular wires **14a** and **14b** have emission maxima at 574 nm in DMSO in each case with quantum yields of 0.012 and 0.014, respectively (Table 1). Addition of micromolar quantities of lithium perchlorate enhanced the quantum yield of **14a** to 0.023, with a 95% enhancement, whereas, **14b** showed only a 21% enhancement. This observation indicates that **14a** is more sensitive to Li^+ compared to **14b.**

The fluorescence enhancement of **14a** and **14b** could be analysed using the Benesi Hildebrand equation,

$$\frac{1}{\Phi_f^0 - \Phi_f} = \frac{1}{\Phi_f^0 - \Phi_f'} + \frac{1}{K_S\,(\Phi_f^0 - \Phi_f')\,[M^+]}$$

where, Ks is the stability constant, Φ_f^o is the quantum yield in the absence of metal ions, Φ_f' is the quantum yield of fluorescence in the presence of the metal ions, Φ_f is the observed quantum yield of fluorescence and $[M^+]$ is the concentration of the metal ions. A plot of $1/\Phi_f^o - \Phi_f$ versus the reciprocal of the metal ion concentration is shown in Figure 11, which is found to be linear, indicating a 1:1-complexation between the squaraine dye unit and the metal ions. The value for the stability constant is determined from the slope of this plot, which is found to be 3.5×10^5 M^{-1}. As observed in the case of the absorption spectral studies, the model dyes **17a** and **17b** did not show any significant changes in their emission spectra, on addition of lithium perchlorate.

Table 1. Effect of $LiClO_4$ on the photophysical properties of **14a**, **14b** and **17a**.

$LiClO_4$	**14a**		**14b**		**17a**	
	0 μM	40 μM	0 μM	40 μM	0 μM	40 μM
λ_{max} (Abs)	565	570	564	566	583	583
λ_{max} (Em)	574	574	575	575	606	606
Φ_f	0.012	0.023	0.014	0.017	-	-
% enhancement	-	95	-	21	-	-

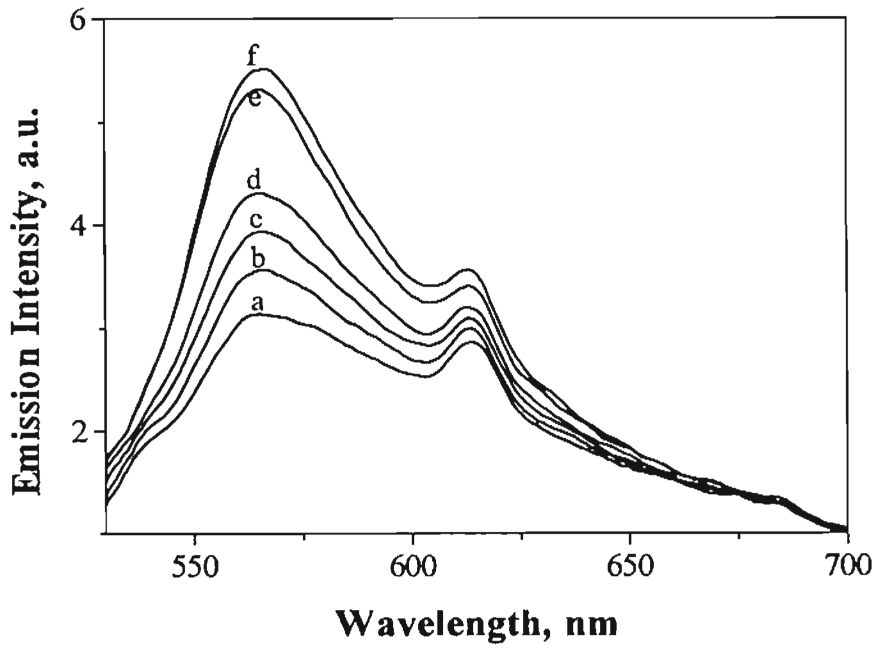


Figure 10. Influence of $LiClO_4$ concentrations on the emission spectrum of **14a** in DMSO. [$LiClO_4$] (a) 0, (b) 4.3, (c) 5, (d) 6, (e) 10, (f) 20 μM.

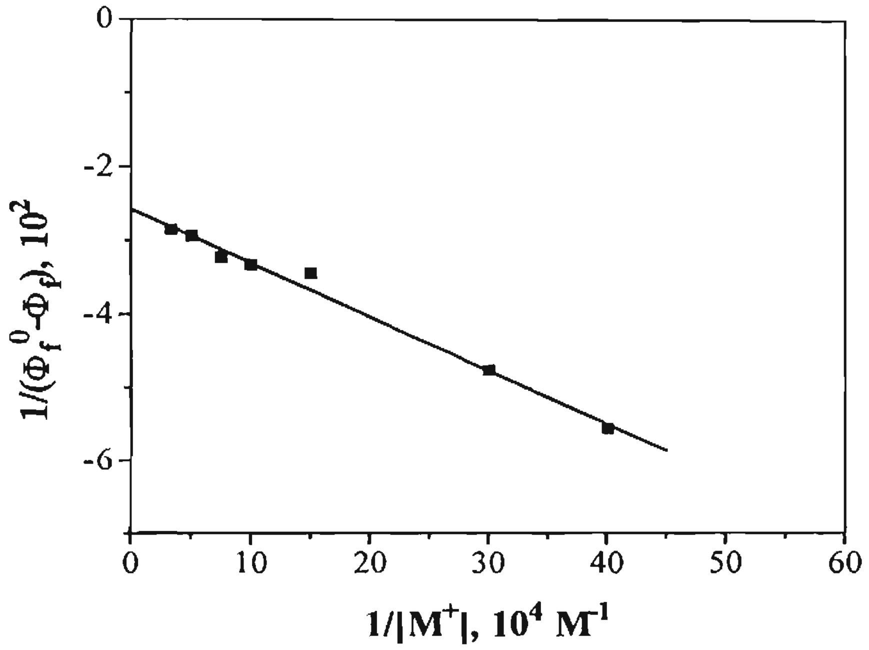


Figure 11. Plot of $1/(\Phi_f^0-\Phi_f)$ versus reciprocal of [Li^+] for the fluorescence enhancement of **14a** in presence of $LiClO_4$.

Addition of sodium perchlorate showed only a marginal effect on emission properties of **14a** and **14b** (Table 2). On the other hand addition of potassium perchlorate to **14b** showed considerable changes to its fluorescence emission intensity and the quantum yield whereas, only minor changes could be noticed for **14a** (Figures 12 and 13). The effects of the addition of potassium perchlorate on the photophysical properties of **14a** and **14b** are shown in Table 3. On addition of a 10 μM solution of potassium perchlorate, a 29% enhancement in the fluorescence quantum yield could be noticed for **14b**. On the other hand, **14a** showed only a 10% enhancement.

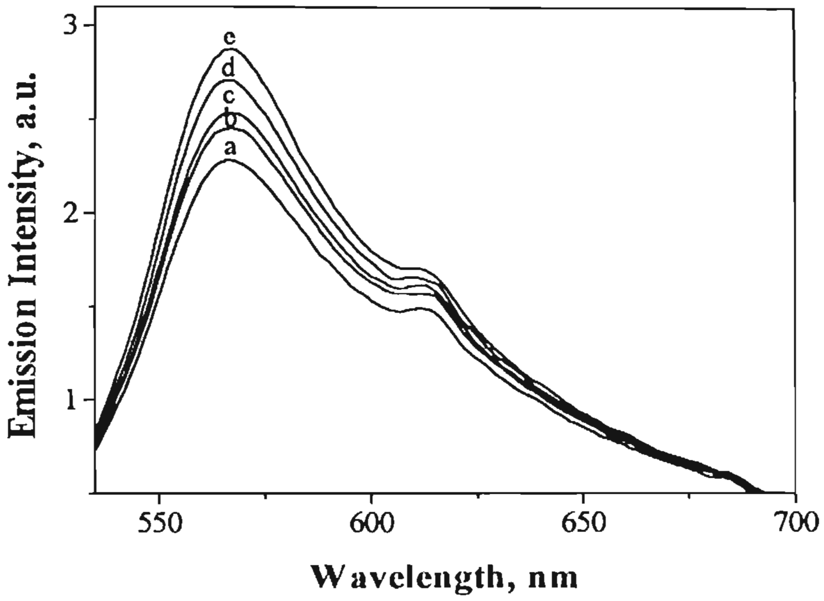


Figure 12. Influence of $KClO_4$ concentrations on the emission spectrum of **14b** in DMSO. $[KClO_4]$ (a) 0, (b) 5, (c) 10, (d) 20, (e) 40 μM.

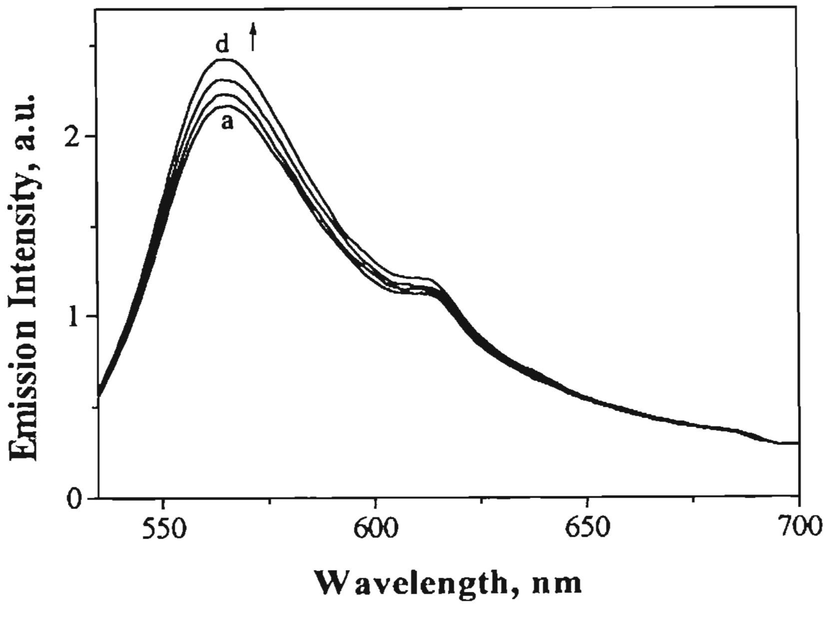


Figure 13. Influence of $KClO_4$ concentrations on the emission spectrum of **14a** in DMSO. $[KClO_4]$ (a) 0, (d) 40 μM.

The stability constant for the complexation of **14b** with potassium ion (Ks = 2.96 x 10^5 M^{-1}) determined from the Benesi-Hildebrand analysis of the emission data. Plot of $1/(\Phi_f^o-\Phi_f)$ versus reciprocal of metal ion concentration showed a linear dependence for potassium perchlorate, indicating a 1:1-complexation (Figure 14).

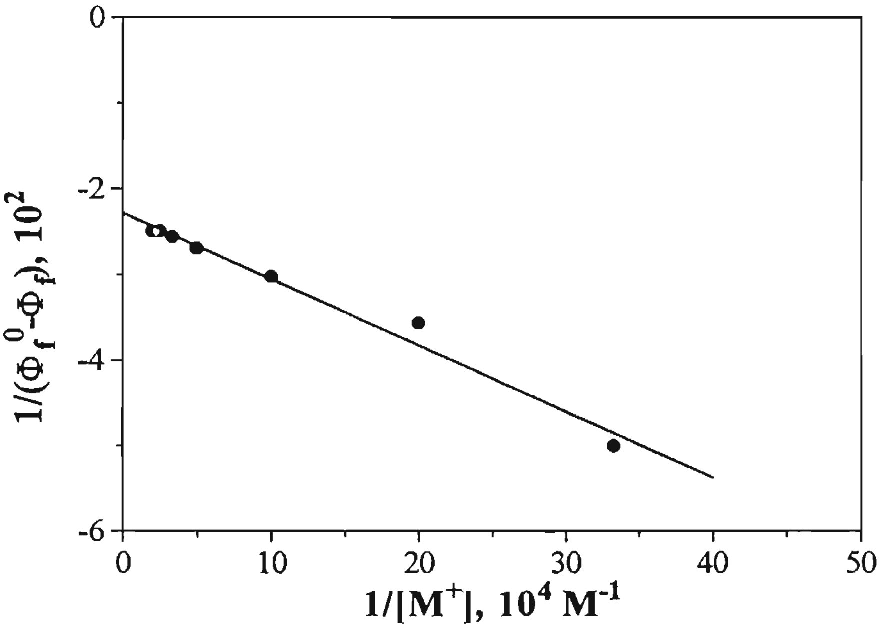


Figure 14. Plot of $1/(\Phi_f^0-\Phi_f)$ versus reciprocal of $[K^+]$ for the fluorescence enhancement o **14b** in presence of $KClO_4$.

The alkali metal ion sensing ability of **14a** is found to be specific for Li^+, compared to Na^+ and K^+ as evidenced from its fluorescence enhancement studies (Figure 15). The squaraine molecular wire **14b** is found to be more selective to K^+, when compared to Li^+ and Na^+ (Figure 16). This selectivity could be explained on

Table 2. Effect of $NaClO_4$ on the photophysical properties of **14a**, **14b** and **17a**.

$NaClO_4$	**14a**		**14b**		**17a**	
	0 μM	40 μM	0 μM	40 μM	0 μM	40 μM
λ_{max} (Abs)	565	570	564	566	583	583
λ_{max} (Em)	574	574	575	575	606	606
Φ_f	0.012	0.013	0.014	0.0143	-	-
% enhancement	-	8	-	2	-	-

Table 3. Effect of $KClO_4$ on the photophysical properties of **14a**, **14b** and **17a**

$KClO_4$	**14a**		**14b**		**17a**	
	0 μM	40 μM	0 μM	40 μM	0 μM	40 μM
λ_{max} (Abs)	565	567	564	570	583	583
λ_{max} (Em)	574	574	575	575	606	606
Φ_f	0.012	0.013	0.014	0.018	-	-
% enhancement	-	10	-	29	-	-

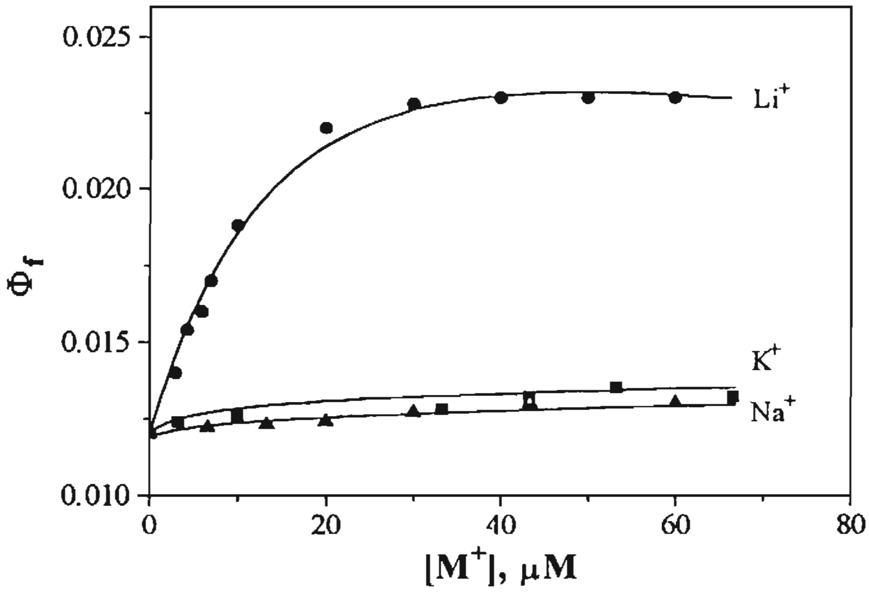


Figure 15. Plot of quantum yield of fluorescence (Φ_f) of **14a** versus metal ion concentration in DMSO.

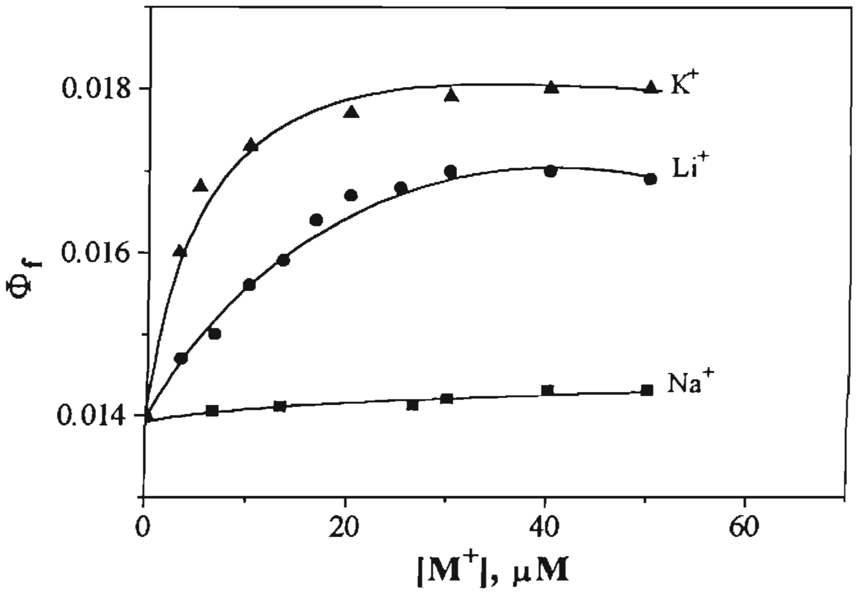
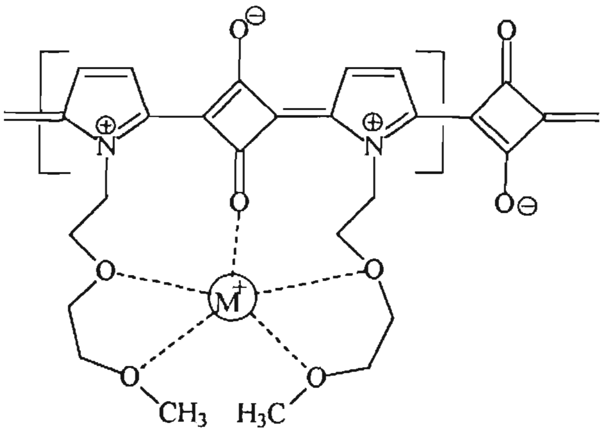


Figure 16. Plot of quantum yield of fluorescence (Φ_f) of **14b** versus metal ion concentration in DMSO.

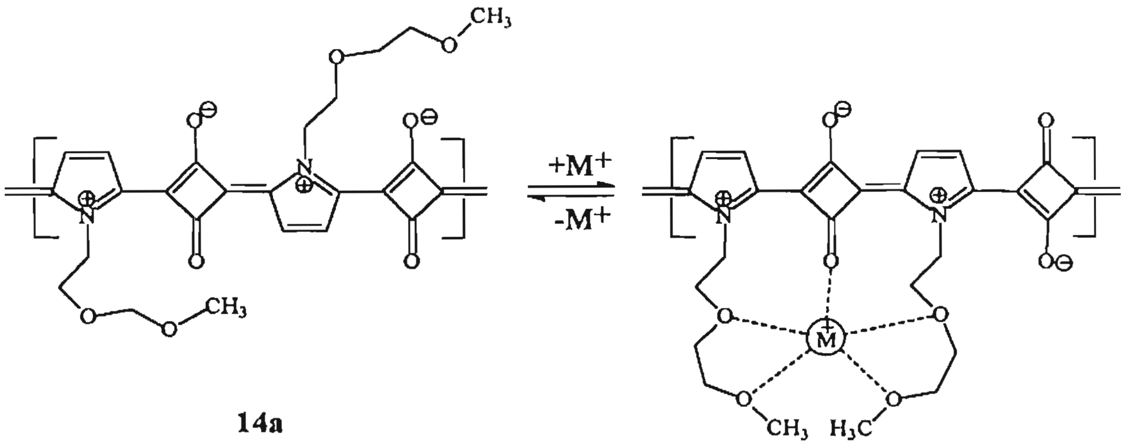
the basis of the oxyethylene chain length (cavity size) and the electron affinity of the metal ions. The calculated stability constant of **14a** for Li^+ is much higher (Ks = 3.5×10^5 M^{-1}) than that of **14b** for Li^+ (Ks = 5.14×10^4 M^{-1}) which indicates a very labile complexation between **14b** and metal ions when compared to **14a**. This observation reveals that the chain length of the oxyethylene moieties is responsible for the observed specificity of **14a** and **14b** towards various alkali metal ions. The 1:1-complex formation obtained from the Benesi-Hildebrand analysis of the emission data reveals that each squaraine dye unit of the squaraine molecular wires complex with a metal ion as represented by the structure **18** (Chart 5).



18

Chart 5

The enhanced response of the squaraine molecular wires **14a** and **14b** when compared to those of the model squaraine dyes **17a** and **17b** can be attributed to the non-planar to planar conformational changes associated with **14a** and **14b**, as shown in Scheme 4. Since the molecular wires **14a** and **14b** have extended π-conjugated backbones, even a small perturbation on their conformation can bring about large changes to their optical properties. On the other hand, such effects are expected to be minimal in the case of the model dyes **17a** and **17b**. In this context it is interesting to compare the metal ion sensing property of a squaraine fluoroionophore **10**, reported earlier by Das *et al.*[31] The azacrown ether attached squaraine dye **10** is capable of detecting millimolar quantities of alkali metal ions. Even though the absorption and emission maxima of **10** remain unchanged, significant quenching of the fluorescence emission could be observed on metal ion complexation. This is attributed to the participation of the lone pair of electrons of the nitrogen atom to metal ion complexation which will reduce the charge-transfer character of **10**. As a result, easier free rotation of the bond between the central C_2O_4 unit and the phenyl ring containing the metal ion becomes possible, leading to enhancement in the nonradiative decay process and consequently decrease in the fluorescence intensity. In contrast, in the case of the squaraine molecular wires



14a
nonplanar

19a
planar

Scheme 4

14a and **14b** and their model squaraine dyes **17a** and **17b**, no such effect is possible. Therefore, the observed fluorescence enhancement in **14a** and **14b** is ascribed to the conformational changes associated with the metal ion complexation.

4.3. Conclusions

Two new squaraine dye based molecular wires **14a** and **14b** containing pendent oxyethylene chains and their model squaraine dyes **17a** and **17b** have been synthesized. The zwitterionic structures of the molecular wires are substantiated by comparing their IR and NMR spectral data with those of **17a** and **17b**. The comparable optical spectral changes induced by the polarity and the hydrogen bonding ability of various solvents support the structural similarities between **14a,b** and **17a,b**. The squaraine dye based molecular wires showed remarkable changes in their emission properties upon metal ion complexation, which make them useful as alkali metal ion sensors. The fluorescence enhancement of the molecular wires, on metal ion complexation is attributed to a non-planar to planar conformational change. The enhanced sensitivity of the squaraine molecular wires, compared to the model squaraine dyes can be explained on the basis of the extended conjugation of the molecular wires. Thus individual molecular entities when wired in series show collective enhanced response on metal ion binding.

4.4. Experimental Section

The IR spectra were recorded on a Perkin Elmer model 883 Infrared spectrometer. The electronic absorption spectra were recorded on a GBC double beam UV-visible spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Jeol EX90, spectrometer using tetramethylsilane (TMS) as internal standard. Elemental analyses were performed on a Perkin Elmer 2400 CHN Elemental

Analyser. Quantum yields of fluorescence were measured by the relative method using optically dilute solutions with Rhodamine 6G (Φ_f = 0.9) in ethanol as reference. Corrections have been made in fluorescence quantum yield measurements for the changes in the absorbance at the excitation wavelength. Spectroscopic solvents were used throughout. For metal binding studies, anhydrous metal perchlorates and dried solvents were used.

Pyrrole (SRL, India) was distilled and kept under nitrogen atmosphere before use. 2,4-Dimethylpyrrole (27%), triethylene glycol monomethyl ether (95%), diethylene glycol monomethyl ether (99%) and squaric acid (98%) were purchased from Aldrich and were used without further purification. All other reagents and solvents were locally purchased and purified according to literature procedures, wherever it was necessary.

4.4.1. Preparation of 2-(methoxyethoxy)ethyl bromide (12a)

A dry, nitrogen-purged flask was charged with diethyl ether (100 mL) and diethylene glycol monomethyl ether (**11a**) (5.9 mL, 50 mmol), and the mixture was cooled to 0 °C. To this solution was added dropwise phosphorous tribromide (2.4 mL, 25 mmol). After the addition, the reaction mixture was stirred at 0 °C for 10 min. To this solution, methanol (7 mL) was added and the reaction mixture was allowed to warm to room temperature. The stirring was continued for 30 min and the reaction mixture was poured into water (10 mL). The organic phase was separated and the aqueous phase was extracted with ethyl acetate (5 x 10 mL). The combined organic phases were washed with 5% sodium bicarbonate (1 x 10 mL) and brine (1 x 10 mL) and dried over sodium sulfate. The solvent was removed *in vacuo* to afford 6.5 g (71%) of the title compound as a colourless clear liquid. IR ν_{max} (neat) 2890, 1463, 1361, 1270, 1201, 1116, 981 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 3.35 (3 H, s, CH_3), 3.4-3.7 (6 H, m, CH_2), 3.75 (2 H, t, J = 6.3 Hz,

CH_2Br); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 29.86, 58.68, 70.08, 70.8, 71.54; Mass spectrum m/z 183 (M^++1, 8), 181 (9), 153 (16), 151 (17), 109 (97), 107 (100), 89 (40), 87 (9).

4.4.2. Preparation of 2-[(methoxyethoxy)ethoxy]ethyl bromide (12b)

Compound **12b** (7.5 g, 67%) was prepared from triethylene glycol monomethyl ether (8 mL, 50 mmol) and phosphorous tribromide (2.4 mL, 25 mmol) employing the same procedure used for the preparation of 2-(methoxyethoxy)ethyl bromide. IR ν_{max} (neat) 2870, 1450, 1351, 1278, 1198, 112, 1025 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 3.36 (3 H, s, CH_3), 3.42-3.72 (10 H, m, CH_2), 3.78 (2 H, t, J = 6.3 Hz, CH_2Br); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 30.07, 42.39, 58.74, 70.35, 71.00, 71.18, 71.75; Mass spectrum m/z 228 (M^++1, 7), 226 (8), 181 (9), 153 (16), 151 (17), 109 (97), 10.7 (100), 89 (40), 87 (9).

4.4.3. Preparation of N-[(methoxyethoxy)ethyl]pyrrole (13a)

A nitrogen-purged flask equipped with a reflux condenser was charged with methylene chloride (10 mL), tetrabutylammonium bromide (3.71 g, 11.5 mmol), pyrrole (79 mL, 11.5 mmol), and 2-(methoxyethoxy)ethyl bromide (1.93 g, 10.52 mmol), and the mixture was cooled to 0 °C using an ice bath. To this solution was added dropwise 50% sodium hydroxide (10 mL). After the addition, the reaction mixture was heated to reflux and allowed to stir for 24 h. The mixture was cooled and diluted with water (5 mL), and the aqueous phase was extracted with ethyl acetate (5 x 5 mL). The combined organic extracts were washed with 3 N hydrochloric acid (1 mL) and dried over sodium sulfate. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography (silica gel, ether/hexane (9:1)) to afford 1.2 g (67%) of the title compound as an yellow liquid, bp 103-110 °C/15 mm. IR ν_{max} (neat) 3098, 2871, 1503, 1450, 1347, 1280, 1196, 934, 848, 725 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 3.35 (3 H, s, CH_3), 3.45-

3.8 (6 H, m, CH_2), 4.05 (2 H, t, J = 5.6 Hz, NCH_2), 6.11 (2 H, t, J = 2.1 Hz, aromatic), 6.68 (2 H, t, J = 2.1 Hz, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 42.48, 58.89, 70.44, 71.27, 71.78, 107.99, 120.86; Mass spectrum m/z 169 (M^+, 55) 137 (13), 124 (5), 111 (30), 94 (30), 80 (100), 67 (20).

4.4.4. Preparation of N-[[(methoxy ethoxy)ethoxy]ethyl]pyrrole (13b)

This compound (1.45 g, 64%) was prepared from 2.38 g (10.52 mmol) of 2-[(methoxyethoxy)ethyl]bromide and 0.77 g (10.52 mmol) of pyrrole using the same procedure described for the preparation of 4-[(methoxyethoxy)ethyl]pyrrole. IR ν_{max} (neat) 3099, 2873, 1500, 1450, 1348, 1282, 1195, 1108, 934, 847, 723 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 3.36(3 H, s, CH_3), 3.61-3.50 (8 H, m, CH_2), 3.72 (2 H, t, J = 5.6 Hz, OCH_2), 4.04 (2 H, t, J = 5.6 Hz, NCH_2), 6.11 (2 H, t, J = 2.1 Hz , aromatic), 6.68 (2 H, t, J = 2.1 Hz); ^{13} C NMR ($CDCl_3$, 22.5 MHz) δ 49.66, 59.23, 70.75, 70.80, 70.85, 71.50, 72.15, 108.28, 121.19; Mass spectrum m/z 213 (M^+, 15), 181 (3), 155 (15), 138 (9), 125 (6), 111 (20), 94 (47), 80 (100), 67 (31).

4.4.5. Preparation of N-[(methoxyethoxy)ethyl]pyrrole-co-squaric acid (14a)

A dry, nitrogen purged flask was charged with 20 mL of 1-butanol and 10 mL of benzene, 0.34 g (2 mmol) of N-[(methoxyethoxy)ethyl]pyrrole and 0.22 g (2 mmol) of squaric acid. The reaction mixture was refluxed for 12 h and the water formed was removed azeotropically. The reaction mixture was concentrated and the pasty liquid was poured into excess of petroleum ether. The precipitated product was filtered, washed with hexane, and dissolved in the minimum amount of DMSO. The DMSO solution was poured into hexane, the precipitated product was filtered, washed with hexane and diethyl ether. The solid product obtained was extracted thoroughly with methanol and chloroform. The combined extract was dried and the solvent was removed under *vacuo*. The residue obtained was dried in a vacuum oven at 40 °C for 24 h to give 320 mg (62%) of **14a**. IR ν_{max} (KBr) 2878, 1776, 1620, 1519, 1351, 1197, 1106, 846; λ_{max} (DMSO) 565 nm; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 3.3-3.8 (9 H, m, CH_2), 4.80 (2 H, t, NCH_2), 6.20 (1 H, m, br, aromatic); Anal.cacld for ($C_{13}H_{13}NO_4)_n$: C, 63.16; H, 5.26; N, 5.67. Found C, 64.1; H, 5.73; N, 5.04.

4.4.6. Preparation of N-[[(methoxyethoxy)ethoxy]ethyl]pyrrole-co-squaric acid (14b)

The polymer **14b** (0.5 g, 56%) was prepared from 0.63 g (3 mmol) of N-[[(methoxyethoxy)ethoxy]ethyl]pyrrole and 0.33 g (3 mmol) of squaric acid under the same conditions employed for the preparation of polymer **14a**; IR ν_{max} (KBr) 2950, 1782, 1735, 1675, 1628, 567, 1488, 1441, 1299, 1114, 936 cm^{-1}; UV λ_{max} (DMSO) 564 nm; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 3.30-3.80 (13 H, m, CH_2), 4.04 (2 H, t, NCH_2), 6.2 (2 H, m, br, aromatic); Anal. calcd for $(C_{15}H_{17}\,NO_5)_n$: C, 61.85; H, 5.84; N, 4.81; Found: C, 61.2; H, 5.04; N, 5.1.

4.4.7. Preparation of N-[(methoxyethoxy)ethyl]-2,4-dimethylpyrrole (16a)

Compound **16a** (2 g, 67%) was prepared from 1.43 g (15 mmol) of 2,4-dimethylpyrrole and 2.75 g (15 mmol) of 2-(methoxyethoxy)ethyl bromide according to the procedure described for the preparation of 4-[(methoxy ethoxy)ethyl]pyrrole. IR ν_{max} (neat) 2934, 1699, 1562, 1458, 1412, 1199, 1112, 915 cm^{-1} ; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.95 (3 H, s, CH_3), 2.05 (3 H, s, CH_3), 3.35 (3 H, s, CH_3), 3.4-3.75 (6 H, m, CH_2), 3.85 (2 H, t, $J = 2.1$ Hz, CH_2), 5.65 (1 H, s, aromatic), 6.3 (1 H, s, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 11.63, 11.72, 58.89, 70.47, 71.06, 71.21, 71.78, 108.03, 117.39, 117.87, 128.02.

4.4.8. Preparation of N-[[(methoxyethoxy)ethoxy]ethyl]-2,4-dimethylpyrrole (16b)

Compound **16b** (2.5 g, 69%) was prepared from 1.43 g (15 mmol) of 2,4-dimethylpyrrole and 3.4 g (15 mmol) of 2-[(methoxyethoxy)ethoxy]ethyl bromide according to the procedure described for the preparation of 4-[(methoxyethoxy)ethyl]pyrrole. IR ν_{max} (neat) 2933, 1698, 1562, 1453, 1415, 1199, 1115, 912 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ (1.95 CH_3), 2.05 (3 H, s, CH_3), 3.35 (3 H, s, CH_3), 3.4-3.75 (10 H, m, CH_2), 3.85 (2 H, t, J = 2.1 Hz, NCH_2), 5.65 (1 H, s, aromatic), 6.3 (1 H, s, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 11.64, 11.73, 65.89, 69.23, 70.75, 70.80, 70.85, 71.50, 72.15, 108.03, 117.39, 117.86, 128.02.

4.4.9. Preparation of the model dye (17a)

A mixture of 1g (5 mmol) of N-(methoxyethoxy)ethyl-2,4-dimethylpyrrole, 0.29 g (2.5 mmol) of squaric acid, 20 mL of 1-butanol and 10 mL of benzene was refluxed for 6 h under nitrogen and the water formed was removed azeotropically. The reaction mixture was cooled and benzene was removed under vacuum. The reaction mixture was poured into water and extracted with dichloromethane. The solvent was removed and the crude dye was recrystallized from a mixture of petroleum ether and dichloromethane. The crystallized dye was dried in a vacuum oven at 45 °C for 24 h to give 0.8 g (67%) of **17a**, mp 95-96 °C; IR ν_{max} (KBr) 2913, 1714, 1605, 1541, 1457, 1394, 1350, 1215, 1114, 963, 843 cm^{-1} ; UV λ_{max} (CH_3CN) 574 nm (13 800 M^{-1}), DMSO 583 nm (79 700 M^{-1}) ; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 2.35 (6 H, s, CH_3), 2.64(6 H, s, CH_3), 3.29 (6 H, s, OCH_3), 3.42 (8 H, s, OCH_2), 3.67 (4 H, t, J = 4.5 Hz, CH_2), 4.85 (4 H, t, J = 4.5 Hz, NCH_2), 6.04 (2 H, s, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 13.75, 15.18, 47.17, 58.86, 70.47, 71.81, 117.73, 126.62, 139.27, 148.51, 173.96, 176.29; Anal. calcd for $C_{26}H_{36}N_2O_6$: C, 66.10; H, 7.63; N, 5.93. Found: C, 66.22; H, 7.81; N, 5.73.

4.4.10. Preparation of the model dye (17b)

The model dye **17b** 0.9 g (64%) was prepared from 1.2 g (5 mmol) of N-[(methoxyethoxy)ethoxy]ethyl-2,4-dimethylpyrrole and 0.29 g (2.5 mmol) of squaric acid adopting the same procedure reported for the preparation of **17a.** IR ν_{max} (KBr) 2913, 1714, 1606, 1543, 1452, 1394, 1350,1215, 1112,960, 841 cm^{-1}; UV λ_{max} (CH_3CN) 574 nm (13 700), DMSO 583 nm (79 600); ^1H NMR ($CDCl_3$, 90 MHz) δ 2.35 (6 H, s, CH_3), 2.64 (6 H, s, CH_3), 3.29 (6 H, s, CH_2), 3.40 (16 H, s, OCH_2), 3.66 (4 H, t, J = 4.5 Hz, CH_2), 4.85 (4 H, t, J= 4.5 Hz, NCH_2), 6.05 (2 H, s, aromatic); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 13.75, 15.18, 65.86, 70.45, 70.81, 71.82, 72.15, 117.75, 126.65, 139.29, 148.53; Anal. calcd for $C_{30}H_{44}N_2O_8$: C, 64.29; H, 7.86; N, 5.00. Found: C, 64.18; H, 9; N, 5.02.

4.5. References

1. Lehn, J.-M. *Angew. Chem. Int. Ed. Engl.*, **1990**, *29*, 1304.
2. *Fluorescent Chromosensors for Ion and Molecule Recognition*; Czarnik, A. W., ED.; ACS Symposium Series, **538**, American Chemical Society: Washington D,C, **1993**.
3. Fabbrizzi, L.; Poggi, A. *Chem. Soc. Rev.* **1995**, 197.
4. *Supramolecular Chemistry I - Directed Synthesis and Molecular Recognition*; Weber, E.; Springer- Verlag: New York, **1993**.
5. Wrighton, M.S. *Comments Inorg. Chem.* **1985**, *4*, 269.
6. *Molecular Electronic Devices*; Carter, F.L.; Ed.; Marcel Dekker: New York, **1982**.
7. *Molecular Electronic Devices, II*; Carter, F.L.; Ed.; Marcel Dekker: New York, **1987**.
8. Hopfield, J.J.; Onuchic, J. N.; Beratan, D. N. *Science*, **1988**, *241*, 817.
9. Handbook of Conducting Polymers; Skotheim, T. J., ED.; Dekker: New York, **1986**.
10. Thackeray, J.W.; Wrighton, M.S. *J. Phys. Chem.* **1986**, *90*, 6674.
11. Zotti, G. *Synth. Met.* **1992**, *51*, 373.
12. Bauerk, P.; Scheib, S. *Adv. Mater.* **1993**, *5*, 848.
13. Youssoufi, H.K.; Hmyene, M.; Garnier, F.; Delabouglise, D. *J.Chem. Soc., Chem. Commun.* **1993**, 1550.
14. Marsella, M. J.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 12214.
15. Marsella, M. J.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1994**, *116*, 9347.
16. Marsella, M. J.; Carroll, P. J.; Swager,T. M. *J. Am. Chem. Soc.* **1995**, *117*, 9832.

17. Marsella, M.J.; Newland, R. J.; Carroll, P. J.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 9842.

18. Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 7017.

19. Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593.

20. Levesque, I.; Leclerc, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2293

21. Brockmann, T. W.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 7435.

22. Brockmann, T. W.; Tour, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 4437.

23. Fery-Forgues, S.; Le Bris, M.-T.; Guette, J.-P.; Valeur, B. *J. Chem. Soc. Chem. Commun.* **1988**, *384.*

24. Fery-Forgues, S.; Le Bris, M.-T.; Guette, J.-P.; Valeur, B. *J. Phys. Chem.* **1988**, *92*, 6233.

25. Bourson, J.; Pouget, J.; Valeur, B. *J. Phys. Chem.* **1993**, *97*, 4552.

26. Letard, J. F.; Lapouyade, R.; Rettig, W. *Pure and Appl. Chem.* **1993**, *65*, 1705.

27. Thomas, K.J.; Thomas, K.G.; Manojkumar, T.K.; Das, S.; George, M.V. *Proc. Indian Acad. Sci. (Chem. Sci.)*, **1994**, *106*, 1375.

28. Das, S.; Thomas, K.G.; Thomas, K. J.; Kamat, P.V.; George, M.V. *J. Phys. Chem.* **1994**, *98*, 9291.

29. Cramer, L. E.; Spears K.G. *J. Am. Chem. Soc.* **1978**, *100*, 221.

30. Moog, R. S.; Burozski, N. A.; Desai, M. M.; Good, W.R.; Silver, C. D.; Thompson, P.A.; Simon, J. D. *J. Phys. Chem.* **1991**, *95*, 8466.

31. Das, S.; Thomas, K.G.; Ramanathan, R.; George, M.V.; Kamat, P.V.; *J. Phys. Chem.* **1993**, *97*, 13625.

32. Dirk, C.W.; Herndon, W.C.; Cervates- Lee, F.; Selnau, H.; Martinez, S.; Kalameghani, P.; Tan, A.; Campos, G.; Velez, M.; Zyss, J.; Ledoux, I.; Cheng, L.-T. *J. Am. Chem. Soc.* **1995**, *117*, 2214.